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# ELEMENTS OF CHEMISTRY,

INCLUDING THE  
APPLICATIONS OF THE SCIENCE IN THE ARTS.

BY

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DECEMBER, 1847.

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and cobalt, is well marked in the salts which they form with a common acid, and is particularly observable in the double salts of these oxides, such as the sulphate of magnesia and potash, sulphate of zinc and potash, sulphate of copper and potash, which have all six atoms of water and a common form. The sulphates themselves of these bases differ, most of them affecting seven atoms of water of crystallization, while the sulphate of copper affects five; but those with the seven may likewise be crystallized in favourable circumstances with five atoms of water, and then assume the form of the copper salt, thus exhibiting a second isomorphism like the arseniate and phosphate of soda.

The sesquioxides of the same class of metals with alumina and the sesquioxide of chromium, which consist of two atoms of metal and three of oxygen, also afford an instructive example of isomorphism, particularly in their double salts. The sulphate of the sesquioxide of iron with sulphate of potash and twenty-four atoms of water, forms a double salt having the octohedral form of sulphate of alumina and potash, or common alum, the same astringent taste, with other physical and chemical properties so similar, that the two salts can with difficulty be distinguished from each other. The salt is called iron alum, and there are corresponding manganese and chrome alums, neither of which contains alumina, but the sesquioxide of manganese and sesquioxide of chromium in its place, with the proportions of acid and water which exist in common alum. In all these salts another substitution may occur without change of form; namely, that of soda or oxide of ammonium for the potash in the sulphate of potash, giving rise to the formation of what are called soda and ammonia alums.

*Chrome -  
alum.*

*Form common  
alum slightly*

*coloured with*

*chrome alum.*

*Also with*

*nucleus of do.*

Certain facts have been supposed to militate against the principles of isomorphism, which require consideration.

1. It appears that the corresponding angles of crystals reputed isomorphous are not always exactly equal, but are sometimes found to differ two or three degrees, although the errors of observation in good crystals rarely exceed 10' or 20' of a degree. But it has been shewn by Mitscherlich that a difference may exist between the inclinations of two series of similar faces in different specimens of the same salt, of 59'; while it is also known that the angles of a crystal alter sensibly in their relative dimensions with a change of temperature (page 3). The angles of crystals are, therefore, affected in their



values within small limits by causes of an accidental character, and absolute identity in crystalline form may require the concurrence of circumstances which are not found together in the ordinary modes of producing many crystals, which are still truly isomorphous.

The following table exhibits the inequalities which have been observed between the angles of certain isomorphous crystals:—

*Rhomboïdal form.*

<i>The large Compound Rhomboid</i>	Carbonate of manganese (diallogite)	103°
	“ lime (calc-spar)	105° 5'
	“ lime and magnesia (dolomite)	106° 15'
	“ magnesia (giobertite)	107° 25'
	“ iron (spathic iron)	107°
	“ zinc (smithsonite)	107° 40'

*Square prismatic with rhomboidal base.*

Carbonate of lime (arragonite)	116° 5'
“ lead (ceruse)	117°
“ strontian (strontianite)	117° 32'
“ baryta (witherite)	118° 57'
Sulphate of baryta	101° 42'
“ lead (anglesite).	103° 42'
“ strontia (celestine)	104° 30'

2. It appears that the same body may assume in different circumstances two forms which are totally dissimilar, and have no relation to each other. Thus sulphur on crystallizing from solution in the bisulphide of carbon or in oil of turpentine, at a temperature under 100°, forms octohedrons with rhombic bases, but when melted by itself and allowed to cool slowly, it assumes the form of an oblique rhombic prism on solidifying at 232°. These are incompatible crystalline forms, as they cannot be derived from one common form. Carbon occurs in the diamond in regular octohedrons, and in graphite or plumbago in six-sided plates, forms which are likewise incompatible. Sulphur and charcoal have each, therefore, two crystalline forms, and are said to be *dimorphous*, (from  $\delta\iota\varsigma$ , twice, and  $\mu\omicron\rho\phi\eta$ , shape). Carbonate of lime is another familiar instance of dimorphism, forming two mineral species, calc-spar and arragonite, which are identical in composition, but differ entirely in crystalline form.

*Not truly  
rhombic*

*Not truly  
prismatic*

*Not truly  
octahedral*

*Not truly  
prismatic*

*Not truly  
prismatic*

*Not truly  
prismatic*

G. Rose has shewn that the first or second of these forms may be given to the granular carbonate of lime formed artificially, according as it is precipitated at the temperature of the air, or near the boiling point of water. Of its two forms, carbonate of lime most frequently affects that of calc-spar: but carbonate of lead, which assumes the same two forms, and is therefore isodimorphous with carbonate of lime, chiefly affects that of arragonite, and is very rarely found in the other form. Had these carbonates, therefore, been each known only in its common form, their isomorphism would not have been suspected,—an important observation, as the want of isomorphism between certain other bodies may be caused by their being really dimorphous, although the two forms have not yet been perceived. Crystallization in three forms is not unknown: thus titanitic acid is found in three distinct forms, as the minerals rutile, brookite, and anatase.

3. The observation of the isomorphism of bodies is of the greatest value as an indication that they possess a similar constitution, and contain a like number of atoms of their constituents. But it must be admitted that the most perfect coincidence in form is likewise observed between certain bodies which are quite different in composition. Thus bisulphate of potash is dimorphous, and crystallizes in one of the two forms of sulphur (Mitscherlich). Nitrate of potash in common nitre has the form of arragonite, and occurs also, there is reason to believe, in microscopic crystals in the form of calc-spar. Nitrate of soda, again, has the form of calc-spar. Permanganate of baryta and the anhydrous sulphate of soda likewise crystallize in one form. Between the first pair, sulphur and bisulphate of potash, the absence of all analogy in composition is sufficiently obvious, notwithstanding their isomorphism. Between nitrate of potash and carbonate of lime, and between permanganate of baryta and sulphate of soda, there is no similarity of composition, on the ordinary view which is taken of the constitution of these salts, but both of these pairs have been assimilated, in speculative views of their constitution proposed by Mr. Johnston\* in regard to the first pair, and by Dr. Clark† in regard to the second, which merit consideration, although the hypotheses cannot be both correct, as they are based

\* Philosophical Magazine, third series, vol. xii. page 480.

† Records of General Science, vol. iv. page 45.

upon incompatible data. To these may be added, the sulphate of baryta with perchlorate and permanganate of potash:  $\text{BaO}$ ,  $\text{SO}_3$  with  $\text{KO}$ ,  $\text{ClO}_7$  and  $\text{KO}$ ,  $\text{Mn}_2\text{O}_7$ . The sulphide of antimony with sulphate of magnesia:  $\text{Sb S}_3$  with  $\text{MgO}$ ,  $\text{SO}_3 + 7\text{HO}$ . Borax with augite, labradorite and anorthite, quartz and chabasite, mohsite and eudialite, anatase and apophyllite, zircon and wernerite, manganite and prehnite. Copper pyrites,  $\text{Cu Fe S}_2$ , has also the same form as braunite or sesquioxide of manganese,  $\text{Mn}_2\text{O}_3$ . Leucite and analcime both belong to the regular system, and are aluminous silicates of similar composition; but, while the first contains one equivalent of potash, the other contains one equivalent of soda +  $2\text{HO}$ .

The nitrite of lead<sup>+46</sup> has the same octohedral figure as the nitrate of lead, (with two atoms of oxygen less in its acid.)

Of examples of identity of crystalline form without any well-established relation in composition, many others might be quoted, if occurrence in the simple forms of the cube and regular octohedron should be allowed to constitute isomorphism. For example: carbon, sea-salt, arsenious acid, galena, the magnetic oxide of iron, and alum, all occur in octohedrons, although they are no way related in composition. But these simple forms are so common, that they can be held as affording no proof of isomorphism, unless in cases where it is to be expected from admitted similarity of composition, as between the different alums, or between chrome iron and the magnetic oxide of iron,  $\text{Cr}_2\text{O}_3$ ,  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ .

But notwithstanding the occurrence of such apparently fortuitous coincidences in form, isomorphism must still be considered as the surest criterion of similarity of composition which we possess. Truly isomorphous bodies generally correspond in a variety of other properties besides external form. Arsenic and phosphorus resemble each other remarkably in odour, although the one is a metal and the other a non-metallic body, while the corresponding arseniates and phosphates agree in taste, in solubility, in the degree of force with which they retain water of crystallization, and in various other properties. The seleniate and sulphate of soda, with ten atoms of water, which are isomorphous, are both efflorescent salts, and correspond in solubility, even so far as to agree in an unwonted deviation from the usually observed increasing rate of solubility at high temperatures, both salts being more soluble in water at  $100^\circ$  than at  $212^\circ$ . In fact, isomorphism appears to be always accompanied by many



common properties, and to be the feature which indicates the closest relationship between bodies.

It will afterwards appear that the more nearly bodies agree in composition, they are the more likely to act as solvents of each other, or to be miscible in the liquid form. An attraction for each other of the same character is probably the cause of the easy blending together of the particles of isomorphous bodies, and of the difficulty of separating them after they are once dissolved in a common menstruum; such isomorphous salts as the permanganate and perchlorate of potash may, indeed, crystallize apart from the same solution, owing to a considerable difference of solubility; and potash-alum may be purified, in a great measure, by crystallization, from iron-alum, which is more soluble, and remains in the mother-liquor; but most isomorphous salts, such as the sulphates of iron and copper, or the iodide and chloride of potassium, when once dissolved together, do not crystallize apart, but compose homogeneous crystals, which are mixtures of the two salts in indefinite proportions. This intermixture of isomorphous compounds is of frequent occurrence in minerals, and was quite inexplicable, and appeared to militate against the doctrine of combination in definite proportions, till the power of isomorphous bodies to replace each other in compounds was recognized as a law of nature. Thus, in garnet, which is a silicate of alumina and lime,  $\text{Al}_2\text{O}_3, \text{SiO}_3 + 3\text{CaO SiO}_3$ , the alumina is found often wholly or in part replaced by an equivalent quantity of peroxide of iron; while the lime, at the same time, may be exchanged wholly or in part for protoxide of iron, or for magnesia, without the proper crystalline character of the mineral being destroyed. Hence the composition of mineral species is most properly expressed by general formulæ, where a letter, such as R, expresses an equivalent of metal which may be calcium, magnesium, manganese, iron, &c. :—

The Pyroxenes by  $3\text{RO}, 2\text{SiO}_3$ .

The Epidotes by  $3\text{RO}, 2\text{Al}_2\text{O}_3, 3\text{SiO}_3$ .

\*\*\* The various forms of crystals were first happily described by Professor Weiss, of Berlin, by reference to "crystalline axes," which are three straight lines passing through the same point, and terminating in the surfaces or angles of the crystal. The simplest case is that in which the three axes cross each other at right angles, and are equal in length, as represented (fig. 51); *c* being the vertical, and *a* and *b* the two horizontal axes. A crystal is formed by applying planes in three principal ways to these axes.

1. By applying six planes so that each shall be perpendicular to one axis and parallel

to the other two, the hexahedron, or, as it is more commonly termed, the cube (fig. 52), is formed. Here the axes terminate in the centre of each of the six faces of the crystal.

FIG. 51.

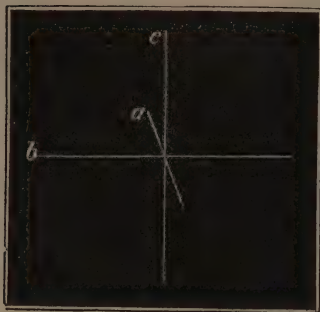
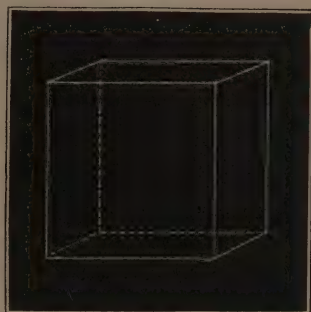


FIG. 52.



2. By applying one plane to an extremity of each of the three axes, as to the points *a*, *b*, and *c* (fig. 51), and seven planes in the same manner to other extremities, the regular octohedron is produced, of which the eight faces or planes are all equilateral triangles (fig. 53). The axes here terminate in the angles of the crystal.

3. The plane may be applied to the extremities of two axes, and be parallel to the third, which will require twelve planes to close the figure, and give rise to the rhombic dodecahedron (fig. 54).

FIG. 53.



FIG. 54.



In these three principal forms, the planes are applied to the axes at equal distances from the centre. They may also cut the axes at unequal distances from the centre, giving rise to four other less usual forms.

A body in crystallizing may assume any of these forms, the only thing constant being the crystalline axes. Hence common salt crystallizes both in the cube and octohedron, although most usually in the former figure; and the magnetic oxide of iron both in the octohedron and rhombic dodecahedron. A body may even assume several of these forms at the same time; that is, may present at once faces of the cube, octohedron, and dodecahedron. Of the octohedral crystals of alum, for instance, the solid angles are always



found to be cut or truncated by planes which belong to the cube of the same axes (fig. 55); and the edges of the octohedron in the same salt are sometimes removed or bevelled by the faces of the dodecahedron (fig. 56). Figure 57 represents a combination of all these three

FIG. 55.



FIG. 56.

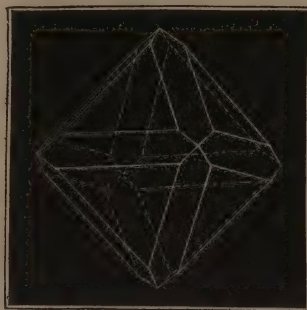


FIG. 57.



forms; and similar or even more complicated combinations are often found in nature.

The groups of forms thus associated, by being deducible from the same axes, constitute what is called a "system of crystallization." Six such systems are enumerated by Weiss, to some one of which every crystalline body belongs.

1. The octohedral or regular system of crystallization, with the three principal axes at right angles to each other, and equal in length. It is that already described.

2. The square prismatic, with the axes at right angles, but two only of them equal in length.

3. The right prismatic, with the axes at right angles, but unequal in length.

4. The rhombohedral, with the axes equal, and crossing at equal but not right angles.

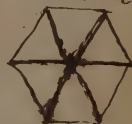
5. The oblique prismatic, with two of the axes intersecting each other obliquely, while the third is perpendicular to both, and unequal in length.

6. The doubly-oblique prismatic, with all three axes intersecting each other obliquely, and unequal.

By the apposition of planes to these different sets of crystalline axes, in the same modes as to the axes of the regular system, series of forms are produced, having a general analogy in all the systems, but specifically different.

For additional information on the subject of crystallography, which, although highly important to the chemical inquirer, is not exactly a department of chemistry, reference may be made to the Essay of Dr. Whewell, in the Phil. Trans. for 1825; to an Essay by Dr. Leeson, in the Memoirs of the Chemical Society, vol. iii.; the German Elements of Crystallography of G. Rose; the Systems of Crystallography of Professor Miller and Mr. J. J. Griffin; and to a short work lately published, entitled "Elements de Cristallographie, par M. J. Müller, traduits de l'Allemand par Jerome Nickles," which appears to be well adapted to the wants of the chemist. A full list of isomorphous substances is given by M. Gmelin in his invaluable *Handbuch der Chemie*, vol. i. p. 83.

4. Rhombic  
3. Incl. Regular  
characterized by 4  
axes, 3 of which are  
equal & cut each  
other at only 60°  
& the 4th axis of a  
different kind, & is  
at right angles to  
the 3 others  
3 axes in  
one plane





*includes*  
Jan. 25 - *crystallography* &c

168 *Isomorphism*

ISOMORPHISM.

*Began*

Jan. 26, 1859, *including Atomic Volume*

*In middle of this subject  
on Monday morn. Jan.  
21, 1850.*

184

CLASSIFICATION OF ELEMENTS.

The extent to which the isomorphous relations of bodies have been traced, will appear on reviewing the groups or natural families in which the elements may be arranged, and observing the links by which the different groups themselves are connected; these classes not being abruptly separated, but shading into each other in their characters, like the classes created by the naturalist for the objects of the organic world.

I. *Sulphur Class*.—This class comprises four elementary bodies: oxygen, sulphur, selenium, tellurium. The three last of these elements exhibit the closest parallelism in their own properties, in the range of their affinities for other bodies, and in the properties of their analogous compounds. They all form gases with one atom of hydrogen, and powerful acids with three atoms of oxygen, of which the salts, the sulphates, seleniates, and tellurates are isomorphous; and the same relation undoubtedly holds in all the corresponding compounds of these elements.

Oxygen has not yet been connected with this group by a certain isomorphism of any of its compounds; but a close correspondence between it and sulphur appears, in their compounds with one class of metals being alkaline bases of similar properties, forming the two great classes of oxygen and sulphur bases, such as oxide of potassium and sulphide of potassium; and in their compounds with another class of elements being similar acids, giving rise to the great classes of oxygen and sulphur acids, such as arsenious and sulpharsenious acids. They farther agree in the analogy of their compounds with hydrogen, particularly of binoxide of hydrogen and bisulphide of hydrogen, both of which bleach, and are remarkable for their instability; and in the analogy of the oxide, sulphide, and telluride of ethyl, and of alcohol and mercaptan, which last is an alcohol with its oxygen replaced by sulphur. This class is connected with the next by manganese, of which manganic acid is isomorphous with sulphuric acid, and consequently manganese with sulphur.

II. *Magnesian Class*.—This class comprises magnesium, calcium, manganese, iron, cobalt, nickel, zinc, cadmium, copper, hydrogen, chromium, aluminum, glucinum, vanadium, zirconium, yttrium, thorium. The protoxides of this class, including water, form analogous salts with acids. A hydrated acid, such as crystallized oxalic acid or the oxalate of water, corresponding with the oxalate of

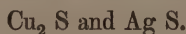
magnesia in the number of atoms of water with which it crystallizes, and the force with which the same number of atoms is retained at high temperatures; hydrated sulphuric acid ( $\text{HO}, \text{SO}_3 + \text{HO}$ ) with the sulphate of magnesia ( $\text{MgO}, \text{SO}_3 + \text{HO}$ ). The isomorphism of the salts of magnesia, zinc, cadmium, and the protoxides of manganese, iron, nickel, and cobalt, is perfect. Water ( $\text{HO}$ ) and oxide of zinc ( $\text{ZnO}$ ) have both been observed in thin regular six-sided prisms; but the isomorphism of these crystals has not yet been established by the measurement of the angles. Oxide of hydrogen has not, therefore, been shewn to be isomorphous with these oxides, although it greatly resembles oxide of copper in its chemical relations. Lime is not so closely related as the other protoxides of this group, being allied to the following class. But its carbonate, both anhydrous and hydrated, its nitrate, and the chloride of calcium, assimilate with the corresponding compounds of the group; while to its sulphate or gypsum,  $\text{CaO}, \text{SO}_3 + 2\text{HO}$ , one parallel and isomorphous compound, at least, can be adduced, a sulphate of iron,  $\text{FeO}, \text{SO}_3 + 2\text{HO}$  (Mitscherlich), which is also sparingly soluble in water, like gypsum. Glucina is isomorphous with lime from the isomorphism of the minerals euclase and zoisite (Brooke).

The salts of the sesquioxide of chromium, of alumina, and glucina, are isomorphous with those of sesquioxide of iron ( $\text{Fe}_2 \text{O}_3$ ), with which these oxides correspond in composition; and the salts of manganic and chromic acids are isomorphous, and agree with the sulphates. The vanadiates are believed to be isomorphous with the chromates. Zirconium is placed in this class, because its fluoride is isomorphous with that of aluminum and that of iron, and its oxide appears to have the same constitution as alumina; and yttrium and thorium, solely because their oxides, supposed to be protoxides, are classed among the earths.

III. *Barium Class.*—Barium, strontium, lead. The salts of their protoxides, baryta, strontia, and oxide of lead, are strictly isomorphous, and one of them at least, oxide of lead, is dimorphous, and assumes the form of lime, and the preceding class in the mineral plumbocalcite, a carbonate of lead and lime (Johnston). But certain carbonates of the second class are dimorphous, and enter into the present class, as the carbonate of lime in arragonite, carbonate of iron in junckerite, and carbonate of magnesia procured by evaporating its solution in carbonic acid water to dryness by the water-bath (G. Rose), which have all the common form of carbonate of strontia. Indeed, these two classes are very closely related.

IV. *Potassium Class*.—The fourth class consists of potassium, ammonium, sodium, silver. The term ammonium is applied to a hypothetical compound of one atom of nitrogen and four of hydrogen ( $\text{NH}_4$ ), which is certainly, therefore, not an elementary body, and probably not even a metal, but which is conveniently assimilated in name to potassium, as these two bodies occupy the same place in the two great classes of potash and ammonia salts, between which there is the most complete isomorphism. Potassium and ammonium themselves are, therefore, isomorphous. The sulphates of soda and silver are similiform, and hence also the metals sodium and silver; but their isomorphism with the preceding pair is not so clearly established. Soda replaces potash in soda-alum, but the form of the crystal is the common regular octohedron; nitrate of potash has also been observed in microscopic crystals, having the arragonitic form of nitrate of soda,\* which is better evidence of isomorphism, although not beyond cavil, as the crystals were not measured. There are also grounds for believing that potash replaces soda in equivalent quantities in the mineral chabasite, without change of form. The probable conclusion is, that potash and soda are isomorphous, but that this relation is concealed by dimorphism, except in a very few of their salts.

This class is connected in an interesting way with the other classes through the second. The subsulphide of copper and the sulphide of silver appear to be isomorphous,† although two atoms of copper are combined in the one sulphide, and one atom of silver in the other, with one atom of sulphur; their formulæ being—



Are then *two* atoms of copper isomorphous with *one* atom of silver? In the present state of our knowledge of isomorphism, it appears necessary to admit that they are.

The fourth class will thus stand apart from the second, which is represented by copper, and also from the other classes connected with the second, in so far as one atom of the present class is equivalent to two atoms of the other classes in the production of the same crystalline form. This discrepancy may be at once removed by halving the atomic weight of silver, and thus making both sulphides

\* Frankenheim, in Poggendorff's *Annalen*, vol. xl. page 447. See also a paper by Professor Johnston on the received equivalents of potash, soda, and silver; *Phil. Mag.* third series, vol. xii. p. 324.

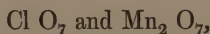
† See *sulphide of silver*, under silver, in this work.



to contain two atoms of metal to one of sulphur. But the division of the equivalents of sodium, potassium, and ammonium, which would follow that of silver, and the consideration of potash and soda as suboxides, are assumptions not to be lightly entertained.

It was inferred by M. Mosander, that lime with an atom of water is isomorphous with potash and soda, because  $\text{CaO} + \text{HO}$  appears to replace  $\text{KO}$  or  $\text{NaO}$  in mesotype, chabasite, and other minerals of the zeolite family. The isomorphism of natrolite and scolezite is so explained:  $\text{NaO}, \text{Al}_2\text{O}_3, 2\text{SiO}_3, 2\text{HO}$  with  $\text{CaO}, \text{Al}_2\text{O}_3, 2\text{SiO}_3, 3\text{HO}$ . On the other hand, it is strongly argued by M. T. Scheerer, that one equivalent of magnesia is isomorphous with three equivalents of water, from the equality of the forms of cordierite and a new mineral aspasolite, the first containing  $\text{MgO}$ , and the second  $3\text{HO}$  in its place; and from a review of a considerable number of aluminomagnesian minerals. One equivalent of oxide of copper, however, is supposed to be replaced by two equivalents of water.\*

V. *Chlorine Class*.—Chlorine, iodine, bromine, fluorine. These four elements form a well-defined natural family. The three first are isomorphous throughout their whole combinations—chlorides with bromides and iodides, chlorates with bromates and iodates, perchlorates with periodates, &c.; and such fluorides also as can be compared with chlorides appear to affect the same forms. The fluoride of calcium <sup>apatite</sup>  $\text{CaF}, 3(3\text{CaO}, \text{PO}_5)$ , is also replaced by the chloride of calcium. It is connected with the second class through perchloric acid; the perchlorates being strictly isomorphous with the permanganates. But the formulæ of these two acids are—



one atom of chlorine replacing two atoms of manganese. Or, this class has the same isomorphous relation as the preceding class to the others; and such I shall assume to be its true relation. Although halving the atomic weight of chlorine, which would give two atoms of chlorine to perchloric acid, is not an improbable supposition, still it would lead to the same strange conclusion as follows the division of the equivalent of sodium,—namely, that chlorine enters into its other compounds, as well as into permanganic acid, always in the proportion of two atoms; for that element is never known to combine in a less proportion than is expressed by its presently re-

\* Poggendorff's *Annalen der Physik und Chemie*, t. lxxviii. p. 319. Also, Millon and Reiset's *Annuaire de Chimie*, 1847, 8vo. Paris, pp. 52 and 234.

ceived equivalent. Cyanogen ( $C_2 N$ ), although a compound body, has some claim to enter this class, as the cyanides have the same form as the chlorides.

VI. *Phosphorus Class*.—Nitrogen, phosphorus, arsenic, antimony, and bismuth; also composing a well-marked natural group, of which nitrogen and bismuth are the two extremes, and of which the analogous compounds exhibit isomorphism. These five elements all form gaseous compounds with three atoms of hydrogen; namely, ammonia, phosphuretted hydrogen, arseniatted hydrogen, &c. The hydriodates of ammonia and of phosphuretted hydrogen are not, however, isomorphous. Arsenious acid and the oxide of antimony, both of which contain three atoms of oxygen to one of metal, are doubly isomorphous. Arsenious acid also is capable of replacing oxide of antimony in tartrate of antimony and potash or tartar emetic, without change of form; and arsenic often substitutes antimony in its native sulphide. The native sulphide of bismuth  $\{Bi S_3\}$  is also isomorphous with the sulphide of antimony ( $Sb S_3$ ). Nitrous acid ( $NO_3$ ), which should correspond with arsenious acid and oxide of antimony, likewise acts occasionally as a base, as in the crystalline compound with sulphuric acid of the leaden chambers. The complete isomorphism of the arseniates and phosphates has already been noticed. But phosphoric acid forms two other classes of salts, the pyrophosphates and metaphosphates, to which arsenic acid supplies no parallels.

This class of elements is connected with the others by means of the following links:—Bisulphide of iron is usually cubic, or of the regular system; but it is dimorphous, and, in spirkise, it passes into another system, and has the form of arsenide of iron;  $Fe S_2$ , or rather  $Fe_2 S_4$ , being isomorphous with  $Fe_2 As S_2$ . Again, bisulphide of iron, in the pentagonal-dodecahedron of the regular system, is isomorphous with cobalt-glance,  $Fe_2 S_4$  with  $Co_2 As S_2$ : so that one equivalent of arsenic appears to be isomorphous with  $2S$ . This is also supported by the isomorphism of the sulphide of cadmium and sulphide of nickel ( $Cd S$  and  $Ni S$ , or  $Cd_2 S_2$  and  $Ni_2 S_2$ ), with the arsenide of nickel ( $Ni_2 As$ ). Tellurium has also been observed in the same form as metallic arsenic and antimony. The phosphorus class approximates also to the chlorine class; nitrogen and chlorine both forming a powerful acid with five equivalents of oxygen, nitric acid, and chloric acid; but of the many nitrates and chlorates which can be compared, no two have proved isomorphous. Nor do the metaphosphates appear at all like the nitrates, although their formulæ correspond.

Nitrogen, it must be admitted, is but loosely attached to this class. It is greatly more negative than the other members of the class, approaching oxygen in that character, with which, indeed, nitrogen might be grouped, N being equivalent to 2O. For while phosphuretted hydrogen is the hydride of phosphorus, or has hydrogen for its negative and phosphorus for its positive constituent, ammonia is undoubtedly the nitride of hydrogen, or has nitrogen for its negative and hydrogen for its positive constituent. The one should be written  $\text{PH}_3$ , and the other  $\text{H}_3\text{N}$ —a difference in constitution which separates these bodies very widely. An important consequence of classing nitrogen with oxygen is, that, in the respective series of compounds of these elements, cyanogen becomes the analogue of carbonic oxide,  $\text{C}_2\text{N}$  being equivalent to CO, or rather  $\text{C}_2\text{O}_2$ .

VII. *Tin Class.*—Tin, titanium. Connected by the isomorphism of titanous acid ( $\text{TiO}_2$ ) in rutile with peroxide of tin ( $\text{SnO}_2$ ) in tin-stone. Titanium is connected with iron and the second class. Ilmenite and other varieties of titanous iron which have the crystalline form of the sesquioxide of that metal,—namely, that of specular iron, and also of corundum (alumina),—are mixtures of a sesquioxide of titanium ( $\text{Ti}_2\text{O}_3$ ) with sesquioxide of iron (H. Rose).

VIII. *Gold Class.*—Gold, which is isomorphous with silver in the metallic state. Gold will thus be connected, through silver, with sodium and the fourth class.

IX. *Platinum Class.*—Platinum, iridium, osmium. From the isomorphism of their double chlorides. The double bichloride of tin and chloride of potassium crystallizes in regular octohedrons, like the double bichloride of platinum and potassium, and other double chlorides of this group; which, although not alone sufficient to establish an isomorphous relation between this class and the seventh, yet favours its existence (Dr. Clark). The alloy of osmium and iridium (Ir Os) is isomorphous with the sulphide of cadmium ( $\text{CdS}$ ) and sulphide of nickel ( $\text{NiS}$ ) (Breithaupt).

X. *Tungsten Class.*—Tungsten, molybdenum, tantalum, niobium, and pelopium. From the isomorphism of the tungstates and molybdates, the salts of tungstic and molybdic acids,  $\text{WO}_3$  and  $\text{MoO}_3$ . Tantalic acid is isomorphous with tungstic acid: tantalite ( $\text{FeO}$ ,  $\text{TaO}_3$ ) with wolfram ( $\text{FeO}$ ,  $\text{WO}_3$ ). So are molybdic and chromic acids, the tungstate of lime, tungstate of lead, molybdate of lead, and chromate of lead (in the least usual of its two forms), being all of the same form. This establishes a relation between molybdic, chromic,



sulphuric, and other analogous acids.\* Niobium and pelopium are introduced into this class as they replace tantalum in the tantalites of Bavaria.

XI. *Carbon Class*—Carbon, boron, silicium. These elements are placed together, from a general resemblance which they exhibit without any precise relation. They are not known to be isomorphous among themselves, or with any other element. They are non-metallic, and form weak acids with oxygen,—the carbonic, consisting of two of oxygen and one of carbon, and the boric and silicic acids, which are generally viewed as composed of three of oxygen to one of boron and silicium. Silicic acid may, perhaps, replace alumina in some minerals, but this is uncertain.

Of the elements which have not been classed, no isomorphous relations are known. They are mercury, which in some of its chemical properties is analogous to silver, and in others to copper, cerium, didymium, lanthanum, lithium, rhodium, ruthenium, palladium, and uranium. Ruthenium, however, is believed to be isomorphous with rhodium, from the correspondence in composition of their double chlorides. Didymium and lanthanum are also probably isomorphous with cerium, as they appear to replace that metal in cerite.

According to the original law of Mitscherlich, that isomorphism depends upon equality in the number of atoms, and similarity in their arrangement, without reference to their nature, the elements themselves should all be isomorphous. Most of the metals crystallize in the simple forms of the cube or regular octohedron, which are not sufficient to establish this relation. But the isomorphism of a large proportion, if not the whole, of the elements may be inferred from the isomorphism of their analogous compounds. Thus from the facts just adduced, it appears that the members of the following large class of elements are linked together from the isomorphism of one or more of their compounds. This large class may be subdivided into smaller classes, between the members of which isomorphism is of more frequent occurrence, and which are then to be viewed as isomorphous groups.

\* Johnston, Phil. Mag. 3d series, vol. xii. p. 387.

## ISOMORPHOUS ELEMENTS.

1. Sulphur.	3. Barium.	<i>With two atoms of the preceding elements.</i>
Selenium.	Strontium.	
Tellurium.	Lead.	
—	—	7. Sodium.
2. Magnesium.	4. Tin.	Silver.
Calcium.	Titanium.	Gold.
Manganese.	—	Potassium.
Iron.	5. Platinum.	<i>Ammonium.</i>
Cobalt.	Iridium.	—
Nickel.	Osmium.	8. Chlorine.
Zinc.	—	Iodine.
Cadmium.	6. Tungsten.	Bromine.
Copper.	Molybdenum.	Fluorine.
Chromium.	Tantalum.	<i>Cyanogen.</i>
Aluminum.	—	—
Glucium.		9. Phosphorus.
Vanadium.		Arsenic.
Zirconium.		Antimony.
		Bismuth.

The tendency of discovery is to bring all the elements into one class, either as isomorphous atom to atom, or with the relation to the others which sodium, chlorine, and arsenic exhibit.

But must not isomorphism be implicitly relied upon in estimating atomic weights, and the alterations which it suggests be adopted without hesitation in every case? Chemists have always been most anxious to possess a simple physical character by which atoms might be recognised; and equality of volume in the gaseous state, equality of specific heat, and similarity in crystalline form, have all in their turn been upheld as affording a certain criterion. The indications of isomorphism certainly accord much better than those of the other two criteria with views of the constitution of bodies derived from considerations purely chemical, and are indeed invaluable in establishing analogy of composition in a class of bodies, by supplying a precise character which can be expressed in numbers, instead of that general and ill-defined resemblance between allied bodies, which chemists perceived by an acquired tact rather than by any rule, and which was heretofore their only guide in classification. Admitting that isomorphism is a certain proof of similarity of atomic constitution within a class of elements and their compounds, it may still be doubted whether the relation of the atom to crystalline form is the same without modification throughout the whole series of the elements, or whether all atoms agree exactly in this or any other physical character.

Crystalline form and the isomorphous relation may prove not to be a reflection of atomic constitution, or immediately and necessarily connected with it, but to arise from some secondary property of bodies, such as their relation to heat; in which a simple atom may occasionally resemble a compound body, as we find sulphur isomorphous in one of its forms with bisulphate of potash; while we find another simple atom, potassium, isomorphous through a long series of compounds with the group of five atoms which constitute ammonium. The occurrence of dimorphism also, both in simple and compound bodies, gives to crystalline form a less fundamental character.

Is it probable that sulphur and carbonate of lime could be made to appear in sets of crystals which are wholly unlike, merely by a slight change of temperature, if form were the consequence of an invariable atomic constitution? Crystalline form, then, may possibly depend upon some at present unknown property of bodies, which may have a frequent and general, but certainly not an invariable relation to their atomic constitution. There may be nothing truly inconsistent with the principles of isomorphism in one atom of a certain class of elements having the same crystallographic value as two atoms of another class, the relation which has been assumed to exist between the sodium, chlorine, and phosphorus classes, and the others, particularly when the classes stand apart, and differ in their properties from all the others, as those of sodium and chlorine do.

#### SECTION V.—ALLATROPY.

Many solid, and a few liquid, bodies admit of a variation of properties, and may present different appearances at the same temperature.

Dimorphism, or the assumption of two incompatible crystalline forms by the same body, in different circumstances, has already been noticed as occurring with sulphur, carbon, carbonates of lime and lead, bisulphate of potash, and chromate of lead. It is also observed in the biphosphate of soda, and in a considerable number of minerals. The sulphate of nickel ( $\text{NiO}$ ,  $\text{SO}_3 + 7\text{HO}$ ) is *trimorphous*; the other salts of similar composition, such as sulphate of magnesia and sulphate of zinc, have been found in two only of these forms. Dimorphous crystals may differ in density,



the densities of calc-spar and arragonite, the forms of carbonate of lime being 2.719 and 2.949, and indeed all resemblance in properties between the crystals may be lost, as in diamond and graphite, the two forms of carbon. The particular form assumed by sulphur and carbonate of lime, which may be made to crystallize in either of their forms at will, is found to depend upon the degree of temperature at which the solid is produced; carbonate of lime being precipitated, on adding chloride of calcium to carbonate of ammonia, in a powder, of which the grains have the form of calc-spar or of arragonite, according as the temperature of the solution is  $50^{\circ}$  or  $150^{\circ}$ .\* A large crystal of arragonite, when heated by a spirit-lamp, decrepitates, and falls into a powder composed of grains of calc-spar. Native carbonate of iron is isodimorphous with carbonate of lime; as spathic iron its specific gravity is 3.872, as junckerite 3.815. The crystals of sulphur produced at the higher of two temperatures become opaque when kept for some days in the air, and pass spontaneously into the other form; while the crystals produced at the lower temperature are disintegrated and changed into the other form by a moderate heat. These observations are important, as establishing a relation between dimorphism and solidification at different temperatures. Red  
Sulphur

A considerable variation of properties is likewise often observable in a solid which is not crystalline, or of which the crystalline form is indeterminate. This fact has been designated *allatropy* by Berzelius (from *ἄλλοτροπος*, of a different nature): dimorphism, or diversity in crystalline form, is, therefore, a particular case of allatropy. Sulphide of mercury obtained by precipitating corrosive sublimate by hydrosulphuric acid, is black; but the same body, when sublimed by heat, or produced by agitating mercury in a solution of the persulphide of potassium, forms cinnabar, of which the powder is the red pigment vermilion; while vermilion itself, if heated till sulphur begins to sublime from it, and then suddenly thrown into cold water, becomes black; although, if allowed to cool slowly, it remains red. Yet it is of the same composition exactly in the black and red states. The iodide of mercury newly sublimed is of a lively yellow colour, and may remain so for a long time; but it generally begins to pass into a fine scarlet on cooling, and may be made to undergo this change of colour in an instant by strongly pressing it: these, however, are two different crystalline forms. The precipitated Spartite &  
Super- & Hydrate  
Spartite

\* G. Rose, Phil. Mag. 3d series, vol. xii. p. 465.

*purpure*  
*i/*  
 sulphide of antimony may be deprived of the water it contains, at the melting point of tin, without losing its peculiar orange colour; but, when heated a little above that temperature, it shrinks, and assumes the black colour and metallic lustre of the native sulphide, without any loss of weight. Again, the black sulphide, when heated strongly and thrown into water, loses its metallic lustre, and acquires a good deal of the appearance of the precipitated sulphide. Chromate of lead, which is usually yellow, if fused and thrown into cold water, gives a red powder. The nitrates of lead are sometimes white, and sometimes yellow; and crystals of sulphate of manganese are often deposited from the same solution, some of which are pink, and others colourless, although identical in composition.

Such differences of colour are permanent, and not to be confounded with changes which are peculiar to certain temperatures: thus oxide of zinc is of a lemon-yellow colour, when strongly heated, but milk-white at a low temperature; the oxide of mercury is much redder at a high than at a low temperature, and bichromate of potash, which is naturally red, becomes almost black when fused by heat. Even bodies in the gaseous state are liable to transient changes of this kind, the brown nitrous fumes being nearly colourless below zero, and on the other hand deepening greatly in colour at a high temperature.

The condition of *glass* is a remarkable modification of the solid form assumed by many bodies. Matter in this state is not crystallized, and on breaking, presents curved and not plain surfaces, or its fracture, in mineralogical language, is *conchoidal*, and not *sparry*. The indisposition to crystallize, which causes solidification in the form of *glass*, is more remarkable in some bodies, such as phosphoric and boracic acids, and their compounds, than in others. The biposphate and binarsenate of soda have the closest resemblance in properties, yet when both are fused by a lamp, the first solidifies on cooling into a transparent colourless glass, and the second into a white opaque mass composed of interlaced crystalline fibres. The phosphate at the same time discharges sensibly less heat than the arseniate in solidifying, retaining probably a portion of its heat of fluidity, or latent heat in a state of combination, while a glass. None of the compounds of silicic acid and a single base, such as soda or lime, or simple silicate, becomes a glass on cooling from a state of fusion, with the exception of the silicate of lead containing a great excess of oxide: they all crystallize. But a *mixture* of the same silicates, when fused, exhibits a peculiar viscosity or tenacity,

*no Main's of  
 Change.*

*Silicic acid  
 in  
 fluids.*

appears to have lost the faculty of crystallizing, and constantly forms a glass. The varieties of glass in common use are all such mixtures of silicates. Glass is sometimes devitrified when kept soft by heat for a long time, owing to the separation of the silicates from each other, and their crystallization; and the less mixed glasses are known to be most liable to this change. It is probable that all bodies differ, when in the vitreous and in the crystalline form, in the proportion of combined heat which they possess, as has been observed of melted sugar (page 45) in these two conditions.

Arsenious acid, when fused or newly sublimed, appears as a transparent glass of a light yellow tint; but left to itself, it slowly becomes opaque and milk white, the change commencing at the surface and advancing to the centre, and often requiring years to complete it, in a considerable mass. The arsenious acid is no longer vitreous, being changed into a multitude of little crystals, whence results its opacity; and it has altered slightly at the same time in density and in solubility. But the passage from the vitreous to the crystalline state may take place instantaneously, and give rise to an interesting phenomenon observed by H. Rose. The vitreous arsenious acid seems to dissolve in dilute and boiling hydrochloric acid without change, but the solution on cooling deposits crystals which are of the opaque acid, and a flash of light, which may be perceived in the dark, is emitted in the formation of each crystal. This phenomenon depends upon and indicates the transition, for it does not occur when arsenious acid already opaque is substituted for vitreous acid, and dissolved and allowed to crystallize in the same manner.

A still greater change than those described, is induced upon certain bodies by exposure to a high temperature, without any corresponding change in their composition. Several metallic peroxides, such as alumina, sesquioxide of chromium and binoxide of tin, cease to be soluble in acids after being heated to redness. The same is true of a variety of salts, such as many phosphates, tungstates, antimonates, and silicates. Many of these bodies contain water in combination, when most readily dissolved by acids, which constituent is dissipated at a high temperature, but in general before the loss of solubility occurs, so that the contained water alone is not the cause of the solubility. Berzelius remarked an appearance often observable when such bodies are under the influence of heat, and in the act of passing from the soluble to the insoluble state. They suddenly glow or become luminous, rising in temperature above the containing



vessel, from a discharge of heat. The rare mineral gadolinite, which is a silicate of yttria, affords a beautiful example of this change. When heated it appears to burn, emits light, and becomes yellow, but undergoes no change in weight. Fluorspar, and many other crystalline substances, exhibit a feeble phosphorescence when heated, which has no relation to this change, and is to be distinguished from it.

The circumstance most certain respecting this change in bodies, which affects so deeply their chemical properties, is that the bodies do not contain a quantity of heat, after the change, which they must have possessed before its occurrence in a combined or latent form. No ponderable constituent is lost, but there is this loss of heat. A change of arrangement of the particles, it is true, must occur at the same time in some of these bodies, such as is observed when sulphite of soda is converted by heat into a mixture of sulphate of soda and sulphuret of sodium, without change of weight; but it would be difficult to apply an explanation of this nature to oxides, such as alumina and binoxide of tin, which contain only two constituents, and still more so to an element such as carbon. The loss of heat observed will afford all the explanation necessary, if heat be admitted as a constituent of bodies equally essential as their ponderable elements. As the oxide of chromium possesses more combined heat when in the soluble than in the insoluble state, the first may justly be viewed as the higher *caloride*, and the body in question may have different proportions of this as well as of any other constituent. But it is to be regretted that our knowledge respecting heat as a constituent of bodies is extremely limited; the definite proportion in which it enters into ice and other solids in melting, and into steam and vapours, has been studied, and also the proportion emitted during the combustion of many bodies, which has likewise proved to be definite. But the influence which its addition or subtraction may have on the chemical properties of a body is at present entirely matter of conjecture. The phenomena under consideration seem to require the admission of heat as a true constituent which can modify the properties of bodies very considerably; otherwise a great physical law must be abandoned, namely, that "no change of properties can occur without a change of composition." But if heat be once admitted as a chemical constituent of bodies, then a solution of the present difficulties may be looked for, for nothing is more certain than that "a change in composition will account for any change in properties." Heat thus combined in definite proportions with bodies, and viewed

as a constituent, must not be confounded with the specific heat of the same bodies, or their capacity for sensible heat, which may have no relation to their combined heat.

#### SECTION VI.—ISOMERISM.

In such changes of properties as have already been described, the individuality of the body is never lost. But numerous instances have presented themselves of two or more bodies possessing the same composition, which are unquestionably different substances, and not mutually convertible into each other. Different bodies thus agreeing in composition, but differing in properties, are said to be *isomeric*, (from *ισος*, equal, and *μερος*, part), and their relation is termed *isomerism*. The discovery of such bodies excited much interest, and they have received a considerable share of the attention of chemists. But the result of a careful study of the bodies associated by similarity of composition, though differing in properties, has been upon the whole unfavourable to the doctrine of isomerism. Isomeric bodies have in general been proved by the progress of discovery to agree in the relative proportion of their constituents only, and to differ either in the aggregate number of the atoms composing them, or in the mode of arrangement of these atoms; and although new cases of isomerism are constantly arising, others are removed as they come to admit of explanation. This is what was to be expected, for isomerism in the abstract is improbable; a difference in properties between bodies, without a difference in their composition, appearing to be an effect without a sufficient cause. Hence, the term isomerism is now generally employed in a limited sense, to indicate simply the identity in composition of two or more bodies as expressed in the proportion of their constituents in 100 parts. Several classes of such isomeric bodies may be formed.

The members of the most numerous class of isomeric bodies differ in atomic weight. Thus we know at present three gases, three or four liquids, and as many solids, which all consist exactly of carbon and hydrogen, in the proportion of one atom to one atom, or, in weight, of 86 parts of carbon and 14 of hydrogen, very nearly. These bodies agree in ultimate composition, but differ completely in every other respect. But a representation of their chemical constitution explains at once the cause of the differences they present, as is obvious

in the following formulæ of four well characterized members of this isomeric group :—

	Equivalents and combining measure.
Olefiant gas . . . . .	$C_4 H_4$ or 4 volumes.
Gas from oil . . . . .	$C_8 H_8$ or 4 volumes.
Naphthene . . . . .	$C_{16} H_{16}$ or 4 volumes.
Cetene . . . . .	$C_{32} H_{32}$ or 4 volumes.

It thus appears that the atom of cetene contains twice as many atoms of carbon and hydrogen as the atom of naphthene, four times as many as the atom of the gas from oil, and eight times as many as the atom of olefiant gas; while as the atom of all these bodies affords the same measure of vapour, or four volumes, they must differ as much in density as they do in the number of their constituent atoms. It is not surprising, therefore, that they all possess different and peculiar properties. Several groups of bodies might be selected from the Table at page 149, which have a similar relation to each other, the number of their atoms being different, although their relative proportion is the same : such as—

Oil of lemons . . . . .	$C_{10} H_8$
Oil of turpentine . . . . .	$C_{20} H_{16}$
and,	
Napthaline . . . . .	$C_{20} H_8$
Paranapthaline . . . . .	$C_{30} H_{12}$

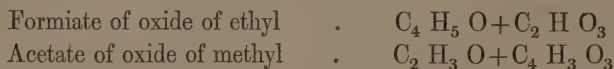
A still more remarkable case is presented by alcohol and the ether ~~from~~ wood-spirit, in which there is identity of condensation as well as of composition, with different equivalents. The vapours of these two liquids have in fact the same specific gravity, and contain, under equal volumes, equal quantities of carbon, hydrogen, and oxygen. But we know that they are of a different type, alcohol being the hydrated oxide of ethyl, and ether of wood-spirit the oxide of methyl, so that their constitution and rational formulæ are quite different :—

Alcohol . . . . .	$C_4 H_5 O + HO$ .
Ether of wood-spirit . . . . .	$C_2 H_3 O$ .

In another class of isomeric bodies, the atomic weight may be equal, as well as the elementary composition. A pair belonging to this class are known, which coincide besides in the specific gravity of their vapours. The composition and atom of both the formate of the oxide of ethyl (formic ether) and the acetate of oxide of methyl,



may be represented by  $C_6 H_5 O_4$ : the density of both their vapours is 2574: and what is very remarkable, these bodies in their ordinary liquid state almost coincide in properties, the density of formic ether being 0.916, and that of the acetate of methylene 0.919, (density of water being  $\approx$ ), while the first boils at  $133^\circ$ , and the last at  $136.4^\circ$ . But when acted on by alkalies, their products are entirely different, the one affording formic acid and alcohol, and the other acetic acid and wood-spirit. Each of the isomeric bodies in question contains, indeed, two different binary compounds, and their constitution is truly represented by different formulæ:—



in which the same atoms are seen to be very differently arranged. The term *metameric* has been applied to bodies so related.

The last class of isomeric bodies are of the same atomic weights, but their constitution or molecular arrangement being unknown, their isomerism cannot at present be explained. It can scarcely be doubted, however, that their molecular arrangement is really different.

One pair of such isomeric bodies will illustrate the coincidences observed not at all unfrequently among organic substances. The racemic and tartaric acids, of which the composition is the same, exhibit a similarity of properties, and a parallelism in their chemical characters, that are truly astonishing. These acids are found together in the grape of the Upper Rhine. They differ considerably in solubility, the racemic being the least soluble, so that they may be separated from each other by crystallization; and the racemic acid contains an atom of water of crystallization, which is not found in the crystals of tartaric acid. They form salts which correspond very closely in their solubility and other properties. The bitartrate and biracemate of potash are both sparingly soluble salts: the tartrates and racemates of lime, lead, and barytes<sup>a</sup>, are all alike insoluble. Both acids form a double salt with soda and ammonia, which is an unusual kind of combination. But what is most surprising, crystals of these double salts not only coincide in the proportion of their water and other constituents, and in the composition of their acids, but also in external form, having been observed by Mitscherlich to be isomorphous. A nearer approach to identity could scarcely be conceived than is exhibited by these salts, which are, indeed, the same both in form and composition. The crystallized acids are both

modified in an unusual manner by heat, and form three classes of salts, as phosphoric acid does. The formulæ of both acids in their ordinary class of salts is  $C_8 H_4 O_{10}$  + two atoms of base (Fremy); but by no treatment can the one acid be transmuted into the other. Lastly, every organic acid produces a new acid by destructive distillation, which is peculiar to it, and is termed its pyr-acid. Now racemic and tartaric acid, when destroyed by heat, agree in giving birth to one and the same pyr-acid.

The allatropy of elements has been supposed to throw light upon the multiplication of series of compounds arising from one radical, and the isomerism of certain compounds. Fused sulphur passes through several allatropic conditions as its temperature is raised, in which it is imagined that the equivalent of the element may be doubled, tripled, and even quadrupled by a coalition of so many single atoms and the formation of compound atoms, which are distinguished as  $\alpha$  sulphur,  $\beta$  sulphur,  $\delta$  sulphur,  $\gamma$  sulphur, &c. In the different series of the oxygen acids of sulphur, containing one, two, three, and four equivalents of sulphur, the different allatropic varieties of sulphur are imagined to exist. Silicium in its combustible and incombustible allatropic conditions may thus give rise to different silicic acids, and allatropic borons and tungstens to the isomeric boric and tungstic acids.

SECTION VII.—ARRANGEMENT OF THE ELEMENTS IN COMPOUNDS.

The names of some compounds imply that they contain other compounds, and indicate a certain atomic constitution, while the names of other compounds express no particular arrangement of their constituent atoms, but leave it to be inferred that the atoms are all directly combined together. Thus sulphate of soda implies the continued existence of sulphuric acid and soda in the salt, while nitric acid, or binoxide of hydrogen, supposes no partition of the compound to which it is applied. But it is to be remembered that the original framers of the nomenclature were guided more by facilities of an etymological nature, in constructing such terms, than by views of the constitution of compounds.

Of a binary compound containing single atoms of its constituents, there cannot be two modes of representing the constitution; but where one of the constituents is present in the proportion of two or more atoms, several hypotheses can always be formed of their mode of aggregation. In a series of binary combinations of the same elements,

such as that of nitrogen and oxygen,  $\text{NO}_1$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{NO}_4$ ,  $\text{NO}_5$ , the simplest view has generally been taken, namely, that it is the elements themselves which unite. But in particular cases the chemist is often involuntarily led into another opinion. Thus binoxide of nitrogen is so often a product of the decomposition of nitric acid, that the acid appears more like a compound of that oxide of nitrogen with oxygen, than a compound of nitrogen itself with oxygen. When the binoxide of hydrogen was first discovered by Thénard, he was led by the whole train of its properties to view it as a compound of water and oxygen, into which it is resolved with so much facility, and to name it accordingly *oxygenated water*, which it may be, and not a direct combination of hydrogen and oxygen; or its formula be  $\text{HO} + \text{O}$ , and not  $\text{HO}_2$ . The periodide of potassium, and the other analogous compounds obtained by dissolving iodine in metallic iodides, were first termed *ioduretted iodides* from similar considerations, and the hyposulphites, obtained by dissolving sulphur in sulphites, *sulphuretted sulphites*. It may be doubted whether chemists would return with advantage to any of these expressions, the views of composition which they indicate being uncertain, and not offering a sufficient inducement to depart from the more systematic designations. The binoxide of hydrogen, for instance, may be easily resolved into water and oxygen, not because water pre-exists in it, but because water is a compound of great stability, and is formed when binoxide of hydrogen is decomposed. Nitric acid, also, is as likely to be a compound of quadroxide of nitrogen with an additional atom of oxygen, as of binoxide of nitrogen with three atoms of the same element.

Certain compound bodies, however, have been observed to act the part of a simple body in combination, and can be traced through a series of compounds. The following substances, for instance, may be represented with considerable probability as compounds of carbonic oxide, as in the formulæ:—

- $\text{CO}$ ,    carbonic oxide.
- $\text{CO} + \text{O}$ ,    carbonic acid.
- $\text{CO} + \text{Cl}$ ,    chloroxycarbonic acid.
- $2\text{CO} + \text{O}$ ,    oxalic acid.

Carbonic oxide is said to be the *radical* of this series, a name applied to any compound which is *capable of combining with simple bodies*, as carbonic oxide appears to do with oxygen and chlorine in these compounds. Messrs. Liebig and Wöhler first proved by decisive



experiments that such a radical exists in the benzoic combinations, which may be represented thus :—

$C_{14} H_5 O_2 + O$ , benzoic acid.

$C_{14} H_5 O_2 + H$ , essential oil of bitter almonds.

$C_{14} H_5 O_2 + Cl$ , chloride of benzoyl, &c.

Cyanogen was the first recognised member of the class of compound radicals, of which the number known to chemists is constantly increasing, and which appear to pervade the whole compounds of organic chemistry. In combining with simple bodies, radicals act the part of other simple bodies, such as metals, chlorine, oxygen, &c. which they replace in compounds.

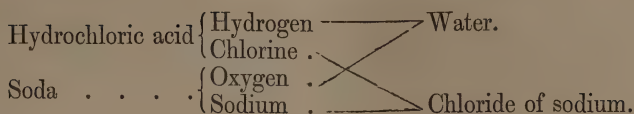
With the elements themselves compound radicals may be divided into two great classes :—

The *Basyl* class, consisting of metals the oxides of which are bases, hydrogen, and the corresponding compound radicals, ammonium, ethyl, &c. These are electro-positive bodies.

The *salt-radical* class—chlorine, sulphur, oxygen, &c., with cyanogen and other compound radicals which combine with metals and other members of the former class, and form salts or compounds partaking of the saline character. Such radicals are also termed *salogens*; they are electro-positive. ~~negative~~

*Constitution of salts*.—Of the supposed combinations of binary compounds with binary compounds, the most numerous and important class are salts. Sulphate of soda is commonly viewed as a direct combination of sulphuric acid and soda, each preserving its proper nature in the compound; and so are all similar compounds of an acid oxide with a basic oxide. An oxygen acid is allowed to exist in them, and they are particularly distinguished as “oxygen-acid salts.” But an opinion was promulgated long ago by Davy, that these salts might be constituted on the plan of the binary compounds of the former class, and their hydrated acids on the plan of a hydrogen acid; a view which is supported by many analogies, and has latterly had a preference given to it by some of our leading chemical authorities. It is, therefore, deserving of serious consideration.

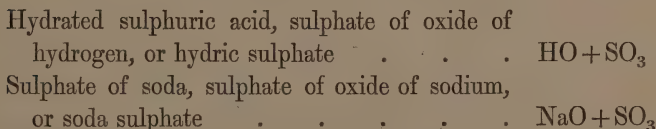
One class of acids, the hydrogen acids, and the salts which they produce with alkalis, are unquestionably binary compounds, and were assumed by Davy as the types of acids and salts in general. Hydrochloric acid is composed of two elements, chlorine and hydrogen, and with soda it forms water and chloride of sodium, thus :—



the hydrogen of the acid being replaced by sodium in the salt formed. Hydrocyanic is another hydrogen acid, of which cyanide of sodium is a salt. In general terms, a *radical* (which may be either simple or compound, like chlorine or cyanogen) forms an *acid* with hydrogen, and a *salt* with sodium or any other metal.

Hydrated sulphuric acid, which consists of sulphuric acid and an atom of water,  $\text{HO} + \text{SO}_3$ , is represented as a hydrogen acid by transferring the oxygen of the water to the sulphuric acid to form a new radical,  $\text{SO}_4$ , which is supposed to be in direct combination with the remaining atom of hydrogen, as  $\text{H} + \text{SO}_4$ . In sulphate of soda, the oxygen of the soda is in the same manner transferred to the acid, or the formula of the salt is changed from  $\text{NaO} + \text{SO}_3$  to  $\text{Na} + \text{SO}_4$ . To  $\text{SO}_4$ , the salt-radical of sulphates, the name *sulphion* has been applied, from the circumstance that, in the voltaic decomposition of a sulphate,  $\text{SO}_4$  travels to the positive pole, and the metal or hydrogen to the negative pole. Its compounds, or the sulphates, become *sulphionides*. The hydrated acid and its soda salt are thus named and denoted on the two views of their constitution—

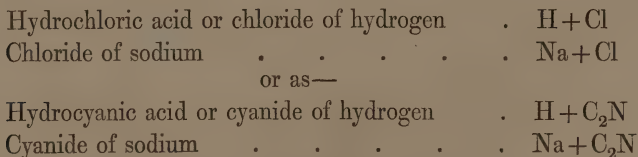
#### I. ON THE ACID THEORY :



#### II. ON THE SALT-RADICAL THEORY :



which last formulæ are strictly comparable with those of an admitted hydrogen acid and its salt, such as—



which thus appear compounds of three different radicals, chlorine (Cl),

cyanogen ( $C_2N$ ), and sulphion ( $SO_4$ ), with the same elementary bodies, hydrogen and sodium. Sulphion is known only in combination, and has not been obtained in a separate state like chlorine and cyanogen. The body, sulphuric acid,  $SO_3$ , which may be separated from some sulphates, and can exist by itself, is looked upon as a product of the decomposition of these salts, and not to pre-exist in them, so that a secondary character is assigned to it.

Hydrated nitric acid, or aqua fortis, becomes a hydrogen acid by the creation of a nitrate radical, nitration. It is the nitrationide of hydrogen instead of the nitrate of water—



The nitrate of potash becomes the nitrationide of potassium, and so of all other nitrates. The existence of nitration is hypothetical, as it has not been insulated; but, in this respect, it is not situated otherwise than nitric acid itself, which cannot be exhibited in a separate state, and is believed to be capable of existing only in a state of combination.

It is evident that the same view is applicable to hydrated oxygen acids in general, which may be made hydrogen acids, by assuming the existence of a new salt-radical for each, containing an atom more of oxygen than the oxygen acid itself, and capable of combining directly with hydrogen and the metals. The class of oxygen acid salts is thus abolished, and they become binary compounds like the chlorides and cyanides. Even oxygen acids themselves can no longer be recognized. It is not sulphuric acid ( $SO_3$ ), but what was formerly viewed as its compound with water, that is the acid, and it is a hydrogen acid. The properties which characterize acids are undoubtedly only observed in the hydrates of the oxygen acids. Thus the anhydrous sulphuric acid does not redden litmus, and exhibits a disposition to combine with salts, such as chloride of potassium and sulphate of potash, rather than with bases. The liquid carbonic acid has little affinity for water, does not combine directly with lime, but dissolves in alcohol, ether, and essential oils, like certain neutral bodies. It is only when associated with water that the bodies referred to exhibit acid properties, and then hydrogen acids may be produced.

On this view, it is obvious that the acid and salt are really bodies of the same constitution, hydrochloric acid being the chloride of hydrogen, as common salt is the chloride of sodium, and sulphuric acid and sulphate of soda being the sulphionides of hydrogen and of



sodium. The acid reaction and sour taste are not peculiar to the hydrogen compound, and do not separate it from the others; the chloride, sulphionide, and nitrationide of copper being nearly as acid and corrosive as the chloride, sulphionide, and nitrationide of hydrogen, and clearly bodies of the same character and composition: they are all equally salts in constitution. The term "acid" is not absolutely required for any class of bodies included in the theory, and might, therefore, be dropped, if it were not that an inconvenience would be felt in having no common name for such bodies as anhydrous sulphuric acid  $\text{SO}_3$ , anhydrous nitric acid  $\text{NO}_5$ , sulphurous acid  $\text{SO}_2$ , carbonic acid  $\text{CO}_2$ , &c. To these substances, which first bore the name, it should now be confined. In considering the generation of salts, three orders of bodies would be admitted, as in the following tabular exposition of a few examples:—

I. The Acid.	II. The Salt-radical.	III. The Salt.
$\text{SO}_3$ . .	$\text{SO}_4$ . .	$\text{SO}_4 + \text{H}$ or a metal.
$\text{NO}_5$ . .	$\text{NO}_6$ . .	$\text{NO}_6 + \text{H}$ or a metal.
	$\text{NC}_2$ . .	$\text{NC}_2 + \text{H}$ or a metal.
	$\text{Cl}$ . .	$\text{Cl} + \text{H}$ or a metal.

The first term of the series, or "the acid," is wanting in the last two examples; and that is the peculiarity of those bodies which constituted the original class of hydrogen acids and their salts: while, to the old class of oxygen acid salts, both an acid and a salt-radical can be assigned, as in the first two examples.

The peculiar advantages of the salt-radical theory are—

First: That, instead of two, it makes but one great class of salts, assimilating in constitution bodies which certainly resemble each other in properties. Chloride of sodium and sulphate of soda are both neutral, and possess a common character, which is that of a soda salt; but they are separated widely from each other on the view of their constitution which is expressed in their names.

Secondly: It accounts for a remarkable law which is observed in the construction of salts; namely, that bases always combine with as many atoms of acid as they themselves contain of oxygen; a protoxide, which contains one atom of oxygen, combining and forming a neutral salt with one atom of an oxygen acid; while an oxide which contains two atoms of oxygen to one of metal, like binoxide of palladium, forms a neutral salt with two atoms of acid; and an oxide of three atoms of oxygen to two of metal, like sesquioxide of iron, forms a

neutral salt with three atoms of acid. The acid and oxygen are thus always together in the exact proportion to form the salt-radical, there being always an atom of oxygen for every atom of acid in the salt. This will appear more distinctly in the following formulæ, which exhibit the composition of the neutral sulphates of a metal in four different states of oxidation, an atom of metal being represented by R :—

FORMULÆ OF NEUTRAL SULPHATES.

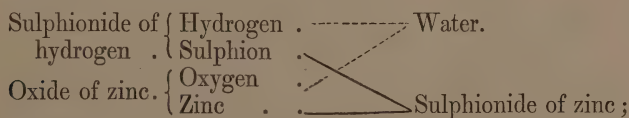
I.	II.	
As consisting of Oxide and Acid.	As consisting of Metal and Salt-radical.	
$RO + SO_3$	$R + SO_4$	as in sulphate of soda.
$R_2O + SO_3$	$R_2 + SO_4$	as in sulphate of sub- oxide of mercury.
$RO_2 + 2SO_3$	$R + 2SO_4$	as in sulphate of bin- oxide of palladium.
$R_2O_3 + 3SO_3$	$R_2 + 3SO_4$	as in sulphate of sesqui- oxide of iron.

The acid is seen in the first column to be always in the proper proportion to form a sulphionide of the metal in the second column; and these sulphionides correspond exactly with known chlorides, such as  $R\ Cl$ ,  $R_2\ Cl$ ,  $R\ Cl_2$ ,  $R_2\ Cl_3$ .

Thirdly: It offers a more simple and philosophical explanation of the action of certain metals upon acid solutions, and of the decomposition of such solutions in other circumstances. Thus when zinc is introduced into hydrochloric acid (chloride of hydrogen), it is allowed on both views, that the metal simply displaces the hydrogen which is evolved, and that chloride of zinc is formed in the place of chloride of hydrogen. In the same way, when zinc is introduced into diluted sulphuric acid, which contains the sulphionide of hydrogen on the binary theory, hydrogen is simply displaced and evolved as before, and the sulphionide of zinc is formed in the place of the sulphionide of hydrogen. The metal in question appears to be incapable of decomposing pure water by displacing its hydrogen at the temperature of the air; but this fact does not interfere with the preceding explanation, as zinc may have a greater affinity for sulphion than for oxygen, and, therefore, be capable of decomposing the sulphionide, but not the oxide of hydrogen. If the acid solution, however, contains sulphate of water, as it does on the old view, then zinc does and does not decompose water; decomposing it when in combination, but not when free. It becomes

necessary to assume that the presence of the acid enhances the affinity of the metal for the oxygen of the water, in a manner which cannot be clearly explained; for the solubility of oxide of zinc in the acid, to which the influence of the acid is often ascribed, accounts for the continuance of the action, by providing for the removal of the oxide, rather than for its first commencement. The phenomena of the decomposition of an acid solution in the voltaic circle, are also most simply explained on the salt-radical theory. Oxide of hydrogen and sulphionide of hydrogen, are both binary "electrolytes," which are decomposed in the voltaic circle in the same manner, although not with equal facility; the common element, hydrogen, proceeding from both to the negative electrode, and oxygen in the one case and sulphion in the other to the positive electrode. The sulphion finds water there, and resolves itself into sulphionide of hydrogen and free oxygen. The decomposition of the sulphionide of sodium or any other salt may be explained in the same simple manner; while on the other view, it must be assumed that a simultaneous transference between the electrodes of acid and alkali with the oxygen and hydrogen of water takes place; and the effect of the acid in promoting the decomposition of the water remains unaccounted for.

When a metallic oxide is dissolved in an acid solution, as oxide of zinc in diluted sulphuric acid, the reaction which occurs is thus explained on the binary theory:



as in the reaction between the same oxide and hydrochloric acid (page 187).

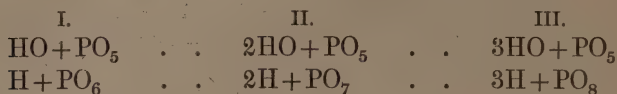
The chief objections to the salt-radical theory, are—

First: The creation of so many hypothetical radicals; namely, one for every class of oxygen-acid salts. But it is to be remembered that the great proportion of oxygen acids, such as nitric, acetic, oxalic, &c. are equally of an ideal character, and cannot be exhibited in a separate state.

Secondly: The peculiarities of the salts of phosphoric acid which are supposed to be inimical to the new view. That acid forms three different and independent classes of salts, containing respectively one, two, and three, equivalents of base to one of acid. On



the binary theory, these three classes of salts must contain three different salt-radicals, combined respectively with one, two, and three equivalents of hydrogen or metal. The three phosphates of water and the corresponding phosphonides of hydrogen would be represented as follows :—



Such salt-radicals and such compounds with hydrogen startle us, from their novelty, but it may be questioned whether they are really more singular than the anormal classes of phosphates, containing several equivalents of base, for which they are substituted, but which we have been more accustomed to contemplate. All the salt-radicals known in a separate state, such as chlorine and cyanogen, combine with one equivalent only of hydrogen, or are monobacylous, but it would be unfair to assume in the present imperfect state of our knowledge that other salt-radicals may not exist, capable of combining with two or three equivalents of hydrogen, as the phosphate-radicals are supposed to do. The existence of at least one such radical is highly probable, as will afterwards appear.

In conclusion, it may be stated that neither view of the constitution of the oxygen-acid salts, (which alone are affected by this discussion), rests on demonstrative evidence; they are both hypotheses, and are both capable of explaining all the phenomena of the salts. But to whichever of them a speculative preference is given, we can scarcely avoid using the language of the acid theory, in the present state of chemical science.

Without deciding definitively in favour of one or other of the rival theories, it is well to keep in view that the great class of salts includes compounds which differ essentially in their capacity of analytical decomposition. A certain number of salts contain salt-radicals which can be isolated, others oxygen-acids which can be isolated, while others have yet afforded neither salt-radical nor acid in a separate state. Hence, they may be classed as—

1. Salts of isolable salt-radicals: chlorides, cyanides, sulphocyanides, &c.

2. Salts of isolable acids: sulphates, carbonates, &c.

3. Salts which contain neither an isolable salt-radical nor an isolable acid: nitrates, acetates, hyposulphites, &c. Even admitting that all salts have the same constitution, the capability of breaking

up in such different ways must affect their modes of decomposition in different circumstances, and produce differences in properties which render such distinctions important.

It has become further necessary to recognize three classes of oxygen-acid salts, which in the language of the acid theory contain one, two, and three equivalents of base to one of acid.

1. *Monobasic salts*.—The great proportion of acids, such as sulphuric, nitric, &c. neutralize but one equivalent of base, or more correctly combine in the proportion of one equivalent of acid to each equivalent of oxygen in the base, and form, therefore, *monobasic salts*. (See formulæ of the neutral sulphates, page 190.) But this is not inconsistent with an acid forming two series of salts with the same base or class of isomorphous bases. Thus there appear to be two well-marked classes of sulphates of the magnesian oxides, which agree in having one equivalent of base, but differ essentially in the proportions of combined water which they affect. In one series the sulphate is combined with one, three, five, or seven equivalents of water. Copperas (a sulphate of iron), Epsom salt (a sulphate of magnesia), blue vitriol (a sulphate of copper), and most of the well-known magnesian sulphates, belong to this class, which may be called the copperas class of sulphates. All the members of it are very soluble in water, and form double salts with sulphate of potash. The other series affect two, four, and six equivalents of water. They are less known, but appear to be of sparing solubility, and to be incapable of forming double salts with sulphate of potash. Gypsum or sulphate of lime belongs to this class, which may, therefore, be called the gypsum class of magnesian sulphates. Sulphate of iron is said to crystallize from solution in sulphuric acid with two equivalents of water, with the crystalline form and sparing solubility of gypsum. Dr. Kane obtained a sulphate of copper with four equivalents of water, by exposing the anhydrous salt to the vapour of hydrochloric acid, which appears to be the second term in this series; and Mitscherlich still maintains the existence of a peculiar sulphate of magnesia containing six equivalents of water of crystallization, which will constitute the third term. It is evident that the cause of such double classes of salts is as deeply seated as that of dimorphism, and hence, possibly, the magnesian sulphate itself, which exists in the two classes, is not the same in its constitution with reference to heat.

2. *Bibasic salts*.—That class of phosphates which received the name of pyrophosphates, was the first in which one equivalent of

acid was found to neutralize two equivalents of base; their formulæ being  $2RO, PO_5$ . The classes of tartrates and racemates which have long been known to chemists, are also bibasic salts. It is the character of a bibasic acid to unite at once with two different bases of the same natural family, which accounts for the formation of Rochelle salt, the tartrate of potash and soda, of which the formula is  $KO, Na O + C_8 H_4 O_{10}$ . It has also been shown that gallic acid is bibasic, the gallate of lead being thus composed:  $2Pb O + C_7 H O_3$ . Now if we attempt to make this a monobasic salt by dividing the equivalents both in base and acid by two, an equivalent of gallic acid would come to contain half an equivalent of hydrogen, which Liebig considers as conclusive against the division of its atomic weight. Itaconic, comenic, euchronic, fulminic, and several other organic bibasic acids, might be named. The compound acids formed by the union of two others, and called copulated acids, such as hypophosphobenzoic acid, are usually of this class.

3. *Tribasic salts*.—The tribasic phosphates of the formula  $3RO, PO_5$ , have likewise proved to be the type of a class of salts. One equivalent of arsenic acid neutralizes three equivalents of base; so, it is probable, does one atom of phosphorous acid. Tannic acid also saturates three atoms of base, the formula of the tannate of lead being  $3PbO + C_{18} H_5 O_9$  (Liebig). There is the same necessity to admit that citric acid is tribasic, and the formula of a citrate  $3RO + C_{12} H_5 O_{11}$ , as there is to allow that gallic acid is bibasic. Most of the citrates contain two equivalents of fixed base and one of water, but the citrate of silver contains three equivalents of oxide of silver. Cyanuric, meconic, camphoric, and several other organic acids, are tribasic.

Two of the three atoms of base in this class of salts may be different, as is observed in certain citrates, cyanurates, and phosphates, or the whole three may be different, as in the phosphate called microcosmic salt, which contains at once soda, oxide of ammonium, and water as bases\*. Two or more of the bases may likewise be isomorphous, or at least belong to the same natural family as soda and oxide of ammonium, water, and magnesia.

*Salts usually denominated Subsals*.—The preceding classes of salts, and many other bodies also, are capable of combining with a certain proportion of water, generally vaguely spoken of as water of crystallization. The compounds of the present class appear to be

\* Inquiries respecting the Constitution of Salts; of oxalates, nitrates, phosphates, sulphates, and chlorides. Phil. Trans. 1837, page 47.



salts which have assumed a fixed metallic oxide in the place of this water. They may, therefore, be truly neutral in composition, the excess of oxide not standing in the relation of base to the acid. It appears that the formulæ of the nitrates named are as follows:—

Nitrate of water (acid of sp. gr. 1.42) .	$\text{HO, NO}_5 + 3\text{HO.}$
Nitrate of copper (prismatic) .	$\text{Cu O, NO}_5 + 3\text{HO.}$
Nitrate of copper (rhomboidal) .	$\text{Cu O, NO}_5 + 6\text{HO.}$
Subnitrate of copper . . . . .	$\text{Cu O, NO}_5 + 3(\text{Cu O, HO}).$

I have distinguished as *constitutional* the three atoms of water which exist in these and all the magnesian nitrates, and which are replaced by three atoms of hydrated oxide of copper in the subnitrate of copper, which is therefore a nitrate of copper, with the addition of constitutional (not basic) oxide of copper; a view which is expressed by the arrangement of the symbols in its formula.

The subnitrates of zinc and lead, and probably also those of nickel and cobalt, have a similar composition (Gerhardt). A similar correspondence is observed between the crystallized neutral sulphate of copper, and the subsulphate of copper, containing four equivalents of oxide of copper, and five of water to one of acid:—

Sulphate of copper,  $\text{CuO, SO}_3, \text{HO} + 4\text{HO.}$

Subsulphate of copper,  $\text{CuO, SO}_3, (\text{CuO, HO}) + 2 (\text{CuO, HO}) + 2\text{HO.}$

Three equivalents of water in the neutral salt appear to be replaced by three equivalents of hydrated oxide of copper in the subsalt. The remaining  $2\text{HO}$  of the latter salt are expelled by a moderate heat, while the other  $4\text{HO}$  in combination with oxide of copper, are extricated by a much higher temperature, and their separation attended by a palpable decomposition of the salt, as it affords a portion of soluble neutral salt afterwards to water. The remark is made by M. Gerhardt, that the number of such subsalts is greatly exaggerated, which is quite in accordance with my own observations; few salts combining with an excess of oxide in more than one or two proportions. Most subsalts are entirely insoluble in water, but when they possess a certain degree of solubility, they may afford other analogous subsalts by double decomposition. Thus a solution of bisubnitrate of lead,  $\text{PbO, NO}_5 + \text{PbO, HO}$ , on the addition of neutral chromate of potash allows the red bisubchromate of lead,  $\text{PbO, CrO}_3 + \text{PbO}$ , to precipitate. M. Gerhardt, who observed this fact, considers that it assimilates the nitrates and pyrophosphates, and indicates that the latter are ordinary subsalts. But this is really a

coincidence of small importance, while nitric acid affords no bibasic hydrate, nor a bibasic salt of soda, as phosphoric acid does.

Water, oxide of copper, oxide of lead, and the hydrates of these metallic oxides, appear to be the bodies most disposed to attach themselves to salts in this manner. The strong alkalies, potash and soda, are never found in such a relation, or discharging any other function than that of base to the acid of the salt. These views of subsalts, in which their constitutional neutrality is preserved, have been extended to organic compounds. Many neutral organic bodies appear to be capable of combining with metallic oxides, particularly with oxide of lead—such as sugar, amidin, dextrin, orcin, and they generally combine with several atoms of the oxide. Thus in the compound of orcin and oxide of lead,  $C_{18} H_7 O_3 + 5PbO$ , the orcin is combined with five atoms of constitutional oxide of lead, which actually replace five atoms of constitutional water, which orcin in its ordinary state contains.

Constitutional water is sometimes replaced by a *salt*, which never happens with basic water. Thus cane sugar may be represented as  $C_{12} H_{11} O_{11}$ , or rather  $C_{24} H_{22} O_{22}$ ; of which one atom of water may be replaced by chloride of sodium, and the compound formed,  $C_{24} H_{21} O_{21} + NaCl$ . It is to be observed that constitutional water is superadded to a salt, and such an element is removed and replaced without affecting the structure of the body to which it is attached. The replacing substance may also be a compound of a very different character from water; for besides metallic oxides and salts, ammonia and certain anhydrous acids appear to be capable of attaching themselves to salts, in the same manner as constitutional water.

A different view of the constitution of subsalts is advocated by M. Millon, who assumes the existence of poly-atomic bases, or that two, three, four, and even six equivalents of water or a metallic oxide, may together constitute a single equivalent of base, and unite as such with a single equivalent of acid to form a neutral salt.\*

*Salts of the type of red chromate of potash.*—Several salts unite with anhydrous acids. Thus both chloride of sodium and chloride of potassium absorb and combine with two atoms of anhydrous sulphuric acid without decomposition, when exposed to the vapour of that substance. Sulphate of potash also combines with one atom of anhydrous sulphuric acid. All these compounds are destroyed by water. But the red chromate of potash, generally called bichromate

\* Annales de Chimie et de Physique, xviii. 333.

of potash, which consists of chromate of potash together with one atom of chromic acid, is possessed of greater stability, as is likewise the compound of chloride of sodium or potassium with two atoms of chromic acid. Another compound containing one atom of potash and three atoms of chromic acid, known as the terchromate of potash, may be viewed as a combination of chromate of potash with two atoms of chromic acid, and represented by  $\text{KO}, \text{CrO}_3 + 2\text{CrO}_3$ . The bichromate of potash will then be  $\text{KO}, \text{CrO}_3 + \text{CrO}_3$ , and the chromate containing chloride of potassium,  $\text{KCl} + 2\text{CrO}_3$ . The biniodate of potash (iodate of water and potash) may be rendered anhydrous, and, when so, is a salt of the same class.

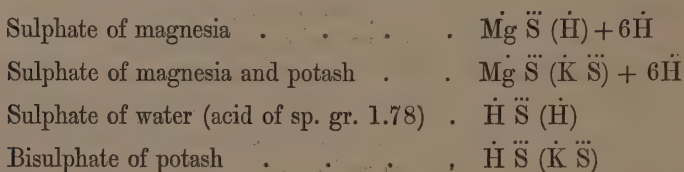
*Double salts.*—Salts combine with each other, but by no means indiscriminately. With a few exceptions, which may be placed out of consideration for the present, the combining salts have always the same acid—sulphates combining with sulphates, chlorides with chlorides. Their bases or their metals, however, must belong to different natural families. Thus it may be questioned whether a salt of potash ever combines with a salt of soda, certainly never with a salt of ammonia. Salts of the numerous metals including hydrogen, belonging to the magnesian family, do not combine together. Thus sulphate of magnesia does not form a double salt with sulphate of lime, with sulphate of zinc, or with sulphate of water; while on the other hand salts of this family are much disposed to combine with salts of the potassium family—sulphate of soda, for instance, forming double salts with sulphate of lime, sulphate of zinc, and sulphate of water. We have thus the means of distinguishing between a double salt, and the salt of a bibasic or tribasic acid. The bisulphate and binoxalate of potash saturated with soda, form sulphates and oxalates of potash and soda, which separate from each other by crystallization, although the acid salts are themselves double salts of water and potash. But the acid fulminate of silver, or the acid tartrate of potash (bitartrate), affords only one salt when saturated with soda, in which isomorphous bases exist, and which, therefore, is a salt of one acid, and not a compound of two salts. The great proportion of the salts which are named *super*, *acid* and *bi*-salts, contain a salt of water, and are double salts—such as the supercarbonate of soda ( $\text{HO}, \text{CO}_2 + \text{NaO}, \text{CO}_2$ ), the bisulphate of potash ( $\text{HO}, \text{SO}_3 + \text{KO}, \text{SO}_3$ ), and the binacetate of soda: but a few of them are bibasic or tribasic salts, containing one or two atoms of water as base—such as the salt called bitartrate of potash, or biphosphate of potash ( $2\text{HO}, \text{KO} + \text{PO}_5$ ).

From these observations must be excepted double salts formed by



fusion, and many salts formed in highly acid solutions, which are scarcely limited in variety of composition; carbonate of potash fusing with the carbonate or sulphate of soda, and sulphate of baryta crystallizing in combination with sulphate of water, from solution in sulphuric acid. Such salts are decomposed by water, and are otherwise deficient in stability, compared with the soluble double salts, to which alone the preceding remarks apply.

There is no parallelism between the constitution of a double salt and that of a simple salt itself, or foundation for the statements which are sometimes made, that one of the salts which compose a double salt has the relation to the other of an acid to a base, and that one salt is electro-negative to the other. The resolution of a double salt into its constituent salts by electricity, has never been exhibited, and is not to be expected, from what is known of electrolytic action; while no analogy whatever subsists between a double salt and a simple salt on the binary view of the constitution of the latter. Besides, the supposed analogy is destroyed by what is known of the derivation of double salts. Sulphate of magnesia acquires an atom of sulphate of potash in the place of an atom of water, which is strongly attached to it, in becoming the double sulphate of magnesia and potash. In the same way, the sulphate of water has an atom of water also replaced by sulphate of potash, in becoming the bisulphate of potash; relations which appear in the rational formulæ of these salts:



It thus appears that a provision exists in sulphate of magnesia itself for the formation of a double salt, and that the molecular structure is unaltered, notwithstanding the assumption of the sulphate of potash as a constituent. The derivation of the acid oxalates likewise throws much light on the nature of double salts. The oxalate of potash contains an atom of constitutional water, which is replaced by hydrated oxalic acid (the crystallized oxalate of water), in the formation of the binoxalate of potash (double oxalate of potash and water), or by the oxalate of copper in the formation of the double oxalate of potash and copper, as exhibited in the following formulæ, in which the replacing substances are enclosed in brackets to mark them as before:

Oxalate of potash . . . . .	$\dot{K} \ddot{C}\ddot{C}, (\dot{H})$
Binoxalate of potash . . . . .	$\dot{K} \ddot{C}\ddot{C}, (\dot{H} \ddot{C}\ddot{C} H_2)$
Oxalate of potash and copper . . . . .	$\dot{K} \ddot{C}\ddot{C}, (\dot{Cu} \ddot{C}\ddot{C} H_2)$

Now the anomalous salt, quadroxalate of potash, is derived in the same way from the binoxalate, as the binoxalate itself is derived from the neutral oxalate, two atoms of water being displaced by two atoms of hydrated oxalic acid, thus :

Binoxalate of potash . . . . .	$\dot{K} \ddot{C}\ddot{C}, \dot{H} \ddot{C}\ddot{C}, (2\dot{H})$
Quadroxalate of potash . . . . .	$\dot{K} \ddot{C}\ddot{C}, \dot{H}\ddot{C}\ddot{C}, (2\dot{H}\ddot{C}\ddot{C}H_2)$

These examples illustrate the derivation of double salts by *substitution*. The structure of the salts, too, exemplifies what may be called *consecutive* combination. The basis of the last mentioned salt, for instance, is oxalate of potash, which is in direct combination with oxalate of water. A compound body is thus produced which seems to unite *as a whole* with two atoms of hydrated oxalic acid. This is very different from the direct combination of all the elements which compose the salt.

In the formation of many other classes of double salts, no substitution is observed, but simply the attachment of two salts together, often of an anhydrous with a hydrated salt, in which case the last often carries its combined water along with it, and sometimes acquires an additional proportion. Thus in the formula of the double chloride of potassium and copper,  $K Cl + Cu Cl, 2HO$ , the formulæ of its constituent salts reappear without alteration; and in that of alum, sulphate of potash is found with the hydrated sulphate of alumina annexed, of which the water is increased from eighteen to twenty-four atoms. In these and all other double salts, the characters of the constituent salts are very little affected by their state of union. If one of them has an acid reaction, like sulphate of alumina or chloride of copper, it retains the same character in combination; and nothing resembling a mutual neutralization of the salts by each other is ever observed. No heat is evolved in their formation. (Memoirs of the Chemical Society, ii. 51).

The compounds of chlorides with chlorides, and of iodides with iodides, are numerous, and were viewed by Bonsdorf as simple salts, in which one of the chlorides is the acid, and the other the base. But such an opinion can no longer be entertained, the chlorides themselves being unquestionably salts, and their compounds, therefore, double salts.

The combinations of such salts with each other as contain different acids are not so well understood, the theory of their formation having hitherto been little attended to. They are in general decomposed by water, and easily, if the solubility of one of their constituents is considerable, as is observed of the compounds of iodate of soda with one and with two proportions of chloride of sodium, of the biniodate of potash with the sulphate of potash, of the oxalate of lime with the chloride of calcium.

The compound cyanides, which form a considerable class of salts, must be excepted from all the preceding general statements in regard to double salts. Cyanides of the same family combine together, as cyanide of iron with cyanide of hydrogen; the compound cyanide also generally consists of three and not of two simple cyanides; and lastly, the properties of compound cyanides are very different from those of the simple cyanides which are supposed to compose them. The simple cyanide of potassium, for instance, is highly poisonous, while the double cyanide of potassium and iron is as mild in its action upon the animal economy as sulphate of soda. But the compound cyanides may be removed from the class of double salts, on a speculative view of their constitution which their anomalous character led me to propose. It is to be premised that the supposed double proto-cyanide of iron and potassium (yellow prussiate of potash) affords no hydrocyanic acid whatever when distilled with an excess of sulphuric acid at a temperature not exceeding  $100^{\circ}$ ; which suggests the idea that it does not contain cyanides or cyanogen. Assuming the existence of a new compound radical,  $N_3 C_6$ , which has three times the atomic weight of cyanogen, and may be called *prussine*, and which is also *tribasylous* or capable of combining with three atoms of hydrogen or metal, like the radical of the tribasic class of phosphates, then the compound cyanides assume a constitution of extreme simplicity. We have one atom of prussine combined always with three atoms of hydrogen or metal in the following salts; in the proto-cyanide of iron and potassium with one of iron and two of potassium; in the compound called ferro-cyanic acid, with one of iron and two of hydrogen; in Mosander's salts, with one of iron, one of potassium and one of barium, calcium, &c.; with two of iron and one of potassium in the salt which precipitates on distilling the yellow prussiate of potash with sulphuric acid at  $212^{\circ}$ . To many of these, parallel combinations might be adduced from the tribasic phosphates. Prussides likewise combine together, producing double prussides, such as



Percyanide of iron and potas-

sium (red prussiate of potash)  $\text{Fe}_2, \text{N}_3 \text{C}_6 + \text{K}_3, \text{N}_3 \text{C}_6$

Prussian blue . . .  $\text{Fe}_2, \text{N}_3 \text{C}_6 + \text{Fe}_3, \text{N}_3 \text{C}_6$

Basic prussian blue . .  $\text{Fe}_2, \text{N}_3 \text{C}_6 + \text{Fe}_3, \text{N}_3 \text{C}_6 + \text{Fe}_2 \text{O}_3$

*Formation of salts by substitution.*—Chemists have come to pronounce less decidedly on theories of the constitution of salts and the arrangement of elements in these and other compounds, since their attention has been fixed upon the formation of compounds, by the substitution of one element for another, without injury to the original form or type, and often to give a preference to empirical over rational formulæ, while their opinions on chemical constitution were suspended. The elementary composition of oil of vitriol, or the hydric sulphate, is expressed by  $\text{SO}_4 \text{H}_2$  the sulphate type, and other neutral sulphates, are formed by replacing the hydrogen by a metal; the zinc sulphate,  $\text{SO}_4 \text{Zn}$ ; the soda sulphate,  $\text{SO}_4 \text{Na}$ . M. Gerhardt, assuming as a law that the equivalent of all compound bodies gives two volumes of vapour, divides the equivalents of the following elements by two—nitrogen, phosphorus, chlorine, hydrogen, and all the metals; and is thereby enabled to construct substitution formulæ, which are often remarkable for their simplicity. This will appear in the following selected formulæ:—

*tra.*

*Jan. 30, 1849*  
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#### FORMULÆ BY M. GERHARDT.

(O=8, S=16; the other symbols = half the usual equivalents.)

##### I. NITRATES.

Hydric nitrate . . .	$\text{NO}_\frac{1}{2} \text{H}$	} Monobasyulous salts.
Magnesia nitrate . . .	$\text{NO}_\frac{1}{2} \text{Mg}$	
Potash nitrate . . .	$\text{NO}_\frac{1}{2} \text{K}$	

$\frac{3}{2}$   
 $\frac{1}{2}$   
 $\frac{3}{2}$

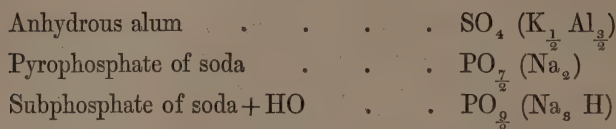
##### II. SULPHATES.

Hydric sulphate . . .	$\text{SO}_4 \text{H}_2$	} Bibasyulous salts.
Magnesia sulphate . . .	$\text{SO}_4 \text{Mg}_2$	
Potash sulphate . . .	$\text{SO}_4 \text{K}_2$	
Potash bisulphate . . .	$\text{SO}_4 \text{KH}$	

##### III. TRIBASIC PHOSPHATES.

Hydric phosphate . . .	$\text{PO}_4 \text{H}_3$	} Tribasyulous salts.
Subphosphate of soda . . .	$\text{PO}_4 \text{Na}_3$	
Phosphate of soda . . .	$\text{PO}_4 \text{Na}_2 \text{H}$	
Biphosphate of soda . . .	$\text{PO}_4 \text{Na} \text{H}_2$	

The preceding groups are symbolized without any division of the equivalents used; but M. Gerhardt departs from this practice, when necessary, in the *unitary* system of notation which he recommends:—



Although a rational formula, strictly speaking, expresses no more than a decomposition,—and the rational formulæ of a compound may truly, therefore, be as numerous as the modes of decomposition of which it is susceptible,—still much would undoubtedly be lost by abandoning such formulæ for formulæ which are entirely empirical; unless, indeed, it is found that the uniform practice of exhibiting the leading constituent, in the proportion of a single equivalent, should bring together different bodies under common formulæ, which are types of useful classification, as M. Gerhardt maintains.

*Salts of Ammonia.*—Ammonia is a gaseous compound of one equivalent of nitrogen and three of hydrogen, of which the solution in water is caustic and alkaline, and which neutralizes acids perfectly, as potash and soda do. But all its oxygen-acid salts contain, besides ammonia, an equivalent of water which is essential to them, and inseparable without the destruction of the salt; and with this additional constituent they are isomorphous with the salts of potash. Hydro-chloric acid also unites with ammonia without losing its hydrogen, and the compound or hydrochlorate of ammonia, which is isomorphous with the chloride of potassium, contains, therefore, an equivalent of hydrogen, besides chlorine and ammonia. On the now generally received theory of these salts, the ammonia with this hydrogen, or that of the water in the oxygen-acid salts, constitutes a hypothetical basyl, *ammonium* ( $\text{NH}_4$ ), to which allusion has already been made as being isomorphous with potassium. This view of the constitution of the salts of ammonia will be made obvious by a few examples:—

#### ON THE AMMONIUM THEORY.

Hydrochlorate of ammonia, $\text{HN}_3, \text{HCl}$ ...	Chloride of ammonium, $\text{NH}_4, \text{Cl}$
Sulphate of ammonia, $\text{NH}_3, \text{HO}, \text{SO}_3$ ...	Sulphate of oxide of ammonium, $\text{NH}_4 \text{ O}, \text{SO}_3$
Nitrate of ammonia, $\text{NH}_3, \text{HO}, \text{NO}_5$ ...	Nitrate of oxide of ammonium, $\text{NH}_4 \text{ O}, \text{NO}_5$

The application of this theory to the compounds of ammonia with hydrosulphuric acid and sulphur is particularly felicitous. These

compounds may be thus represented, and placed in comparison with their potassium analogues,  $\text{NH}_4$  being equivalent to K:—

Sulphide of ammonium . . .	$\text{NH}_4 \text{ S}$	.. KS
Sulphide of ammonium and hydrogen (bihydrosulphate of ammonia) . . .	$\text{NH}_4 \text{ S, HS}$	.. KS, HS
Tritosulphide of ammonium .	$\text{NH}_4 \text{ S}_3$	.. $\text{KS}_3$
Pentasilphide of ammonium .	$\text{NH}_4 \text{ S}_5$	.. $\text{KS}_5$

Ammonium is supposed to present itself in a tangible form, and in possession of metallic characters, in the formation of what is called the *ammoniacal amalgam*. When mercury alloyed with one per cent. of sodium is poured into a saturated cold solution of sal ammoniac (chloride of ammonium), it undergoes a prodigious increase of bulk, expanding sometimes from one volume to two hundred volumes, without becoming in the least degree vesicular, and acquiring a butyraceous consistence, while its metallic lustre is not impaired. A small addition is at the same time made to its weight, estimated at from 1 part in 2000 to 1 in 10,000, which certainly consists of ammonia and hydrogen in the proportions of ammonium. The sodium, it is supposed, combines with the chlorine of chloride of ammonium, and the liberated ammonium with mercury, so that the metallic product is an amalgam of ammonium. It speedily revolves itself again spontaneously into running mercury, ammonia, and hydrogen, unless the temperature be reduced so far as to freeze it. After all, however, neither isolation nor the metallic character is essential to ammonium as an alkaline radical, other basyls being now admitted, such as ethyl and benzoyl, which have no claim to such characters.

Other classes of ammoniacal salts may be formed in which the fourth equivalent of hydrogen in ammonium is replaced by a metal of the magnesian family,—by copper in particular, which most resembles hydrogen. Thus anhydrous chloride of copper absorbs a single equivalent of ammonia with great avidity and the evolution of much heat, which cannot afterwards be separated from it by the agency of heat. The compound appears to be strictly analogous to chloride of ammonium, but contains an equivalent of copper in the place of hydrogen. Its formula is  $\text{NH}_3 \text{ Cu, Cl}$ , and it may be named the chloride of *cuprammonium*. This salt and many others are likewise capable of combining with more ammonia, which is retained less strongly, and has the relation of constitutional water to the salt.



The constitution of these combinations will be more minutely considered in other parts of the work.

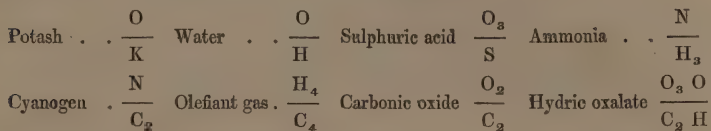
*Amidogen and amides.*—The existence of another compound of nitrogen and hydrogen ( $\text{NH}_2$ ), containing an equivalent less of hydrogen than ammonia, is recognised in an important series of saline compounds, although it has not been isolated. These compounds are called *amides*, and hence the name amidogen applied to their radical. When potassium is heated in ammoniacal gas, the metal is converted into a fusible green matter, which is the amide of potassium, while an equivalent of hydrogen is disengaged. Amidogen exists also in the white precipitate of mercury formed on adding ammonia to corrosive sublimate, the product being a double chloride and amide of mercury ( $\text{Hg Cl} + \text{Hg NH}_2$ ).

Amides are produced in an interesting way, by the abstraction of the elements of water from compounds of ammonia with oxygen acids. Thus, on decomposing oxalate of ammonia by heat, the acid losing a proportion of oxygen, and the ammonia a proportion of hydrogen, *oxamide* sublimes, which consists of  $\text{NH}_2 + 2\text{CO}$ . When ammoniacal gas and anhydrous sulphuric acid vapour are mixed together, a saline substance is produced which dissolves in water, but is not sulphate of ammonia, the solution affording no indications of sulphuric acid. It is believed to be a hydrated *sulphamide*, or to be constituted thus,  $\text{NH}_2, \text{SO}_2 + \text{HO}$ ; a compound which it will be observed contains neither ammonia nor sulphuric acid. Similar products result from the action of ammonia on dry carbonic acid and all the other anhydrous oxygen salts. The difference between these compounds and the true salts of ammonia affords an argument in favour of the ammonium theory of the latter.

#### ANTITHETIC OR POLAR FORMULÆ.

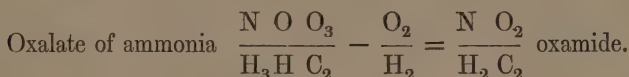
Formulæ for compounds may be constructed to exhibit the attraction of the ultimate elements for each other without involving any contested theory of the constitution of compounds, and which indeed might supersede the consideration of such views, were it not that the nomenclature, which it would be inconvenient to alter greatly, is founded upon the latter. A certain amount of information is given in the ordinary formulæ by the arrangement of the symbols, the symbol of the basylous or positive constituent being placed before the symbol of the halogenous or negative constituent, as in  $\text{HO}$  for

water,  $\text{SO}_3$  for sulphuric acid. To carry out this principle farther, and make its application more perspicuous, I have suggested the writing of a formula in two lines, placing all the negative constituents in the upper, and the positive in the lower line :—

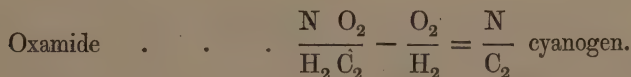


From their construction these formulæ are named *antithetic*, the two orders of constituents being placed opposite or against each other ; or *polar*, from exhibiting the opposite attractive forces of the elements. Several decompositions already referred to, and others, may be made more intelligible by their aid.

*Decomposition of ammoniacal salts.*—In the decomposition of oxalate of ammonia and formation of oxamide, the change consists in the abstraction of two equivalents of water from the constituents of the salt : the formulæ being—



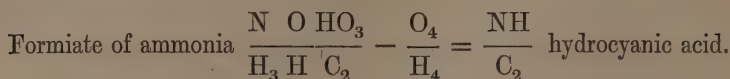
The interesting observation has lately been made by M. Dumas, that by distillation with anhydrous phosphoric acid, four equivalents of water are separated from oxalate of ammonia, and cyanogen formed. Supposing that the formation of oxamide precedes this last decomposition, we have—



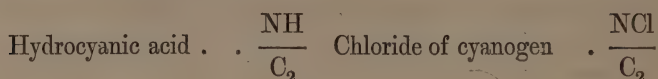
It is seen, that although we cannot say that water exists either in oxalate of ammonia or in oxamide, still 4O is negative and 4H positive in the first of these substances, and 2O negative with 2H positive in the second the relation which these elements bear to each other in water. The polar relation of these elements, therefore, does not require to be subverted, when they are led to unite and take the form of water, under the influence of the attraction of phosphoric acid for that oxide. It is manifestly a law of decomposition that those decompositions take place most readily which permit the elements to continue in their original polar condition and position in the formulæ; the explanation being, that such decompositions are promoted by the

peculiar attractions of the ultimate elements for each other as they exist in the original compound; or the compound molecule is broken up in the direction in which it naturally divides.

The decomposition by phosphoric acid of other salts of ammonia containing acids related to the alcohols, illustrates the same constancy of polar relation in the elements before and after the change. Thus, formiate of ammonia gives hydrocyanic acid by the abstraction of four equivalents of water:—



Here the hydrogen of hydrocyanic acid is represented as negative, and it can certainly be replaced by chlorine, a negative element, and the chloride of cyanogen formed:—

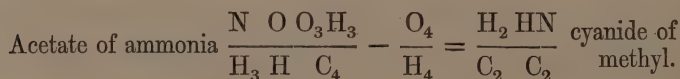


With a metallic oxide, however, hydrocyanic acid gives a cyanide, and then the hydrogen appears positive—

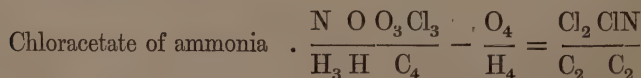


But hydrocyanic acid is in the lowest degree feeble in its powers as an acid, or as cyanide of hydrogen, and its hydrogen appears to be just on the limit between the basylous and halogenous character and position.

Acetate of ammonia distilled with phosphoric acid also loses four equivalents of water, like all the ammoniacal salts in question, and gives the cyanide of methyl:—



The chloracetate of ammonia in losing 4HO gives a liquid body of the composition  $\text{C}_4\text{Cl}_3\text{N}$ :—

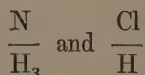


Here the single negative H of hydrocyanic acid is also under the positive attraction of the  $\text{C}_2$  of the hydrocarbon,  $\text{C}_2 \text{ H}_2$ , a cross

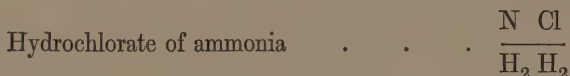


attraction, which forms a bond of union between the hydrocyanic acid and hydrocarbon, and supports the equilibrium.

*Why is ammonia a base ?*—Of ammonia and hydrochloric acid the antithetic formulæ are—



There can be little doubt but that when these bodies are united, the highly negative chlorine shares, or assumes entirely, the positive attraction of the third equivalent of hydrogen in ammonia, which there is reason to believe is less powerfully attracted or neutralized by the negative nitrogen than the other two equivalents of hydrogen. We thus obtain the following formula:—

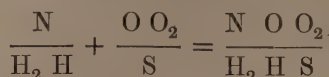


Now the acid character of hydrochloric acid, which is neutralized in the salt, depends upon the former substance being a compound in which a powerful salt-radical, chlorine, is united with a weak basyl, hydrogen. With a powerful basyl, such as potassium, chlorine gives a neutral salt, the chloride of potassium. But it is probable that the subchloride of hydrogen,  $\text{H}_2\text{Cl}$ , if it could exist in a separate state, would be an equally neutral salt, for hydrogen belongs to the magnesian class of elements, two atoms of which appear to be equivalent to one atom of the potassium class, or  $\text{H}_2\text{Cl}$  to be equivalent to  $\text{KCl}$ , and possibly isomorphous with it. One atom of nitrogen there are also grounds for believing to be equivalent in composition to two atoms of oxygen, or  $\text{N} = 2\text{O}$ . Hence the compound  $\frac{\text{N}}{\text{H}_2}$  has

a character of saturation, or polar neutralization, like  $\frac{\text{O}_2}{\text{H}_2}$  or two equivalents of water. In ammonia, therefore, the third basylous atom of hydrogen may well be considered as unsaturated, and to be what imparts a basylous or positive character and activity to the compound. In metallic oxides which are bases, we have also the positive property of the metal imperfectly saturated by the weak negative body oxygen, and the positive attraction therefore in excess.

In the oxygen acids, on the contrary, there is an excess of negative attraction from the predominance of the oxygen element, and it is remarkable that in the more powerful acids, such as sulphuric, nitric, and chloric, one equivalent of this oxygen is but feebly united, and

its negative attraction free to act, like the positive attraction of the third equivalent of hydrogen in ammonia. Hence ammonia and anhydrous sulphuric acid readily combine :—

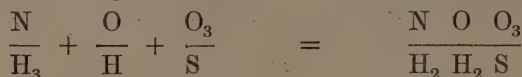


From the action of the affinities exhibited in the last formula, a stable equilibrium results; but it is not intended to express that amidogen, water, and sulphurous acid, exist ready formed in the compound. Indeed, in no case do the formulæ express actual formation of subordinate compounds, or anything more than what are considered to be the predominating set of attractions among all the possible attractions which the elements have for each other, and all of which they continue to exert in some degree.

In sulphate of oxide of ammonium, the affinities of equilibrium are those of the elements of amidogen, suboxide of hydrogen, and sulphuric acid :—

Constituents of Sulphate of Ammonia.

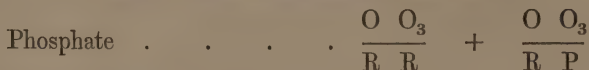
Sulphate of Ammonia.



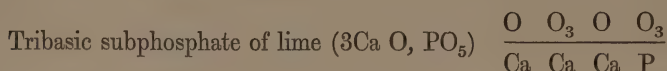
In this and all the other oxygen-acid salts of ammonia, the highly alkaline oxide  $\text{H}_2\text{O}$  appears, and constitutes the point of attachment for the acid. Other sources of stability in the sulphate of ammonia are—first, the attraction of N for its third atom of hydrogen, which is never entirely relinquished, although the latter is more under the influence of the O of the water; and, secondly, the attraction of the  $\text{O}_3$  of the sulphuric acid for the basylous  $\text{H}_2$ : for these cross attractions prevent the division of the compound into subordinate compounds under the influence of the predominating affinities first enumerated. This salt may be taken as a fair example of the assumed mode of formation of compounds, in which the affinities of the elementary atoms only are operative, to the entire exclusion of the affinities usually assigned to subordinate groups of elements acting as compound radicals or quasi-elements.

*Why are arsenic and phosphoric acids tribasic?*—Phosphoric acid,  $\text{PO}_5$ , may be considered, from its properties and mode of formation, as phosphorous acid,  $\text{PO}_3$  + two equivalents of oxygen less strongly combined; and in the same way, arsenic acid,  $\text{As O}_5$ , as arsenious acid,  $\text{As O}_3$  + two equivalents of oxygen. Now, when

united with a base, which we shall suppose a metallic protoxide, RO, these two surplus equivalents of oxygen in the phosphoric acid, added to the single equivalent of oxygen in the base, convert an equivalent of the latter into an acid of the formula  $RO_3$ . Two more equivalents of base are required—one to neutralize this  $RO_3$ , and the other to neutralize the phosphorous acid,  $PO_3$ ; making three equivalents of base to every single equivalent of phosphoric acid. The general formula for a so-called tribasic phosphate is, therefore—



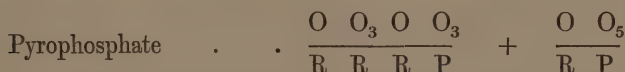
and resembles a double sulphate,  $RO, SO_3 + RO, SO_3$ .



Phosphoric acid appears farther to have the power, when heated strongly, of assuming the two equivalents of oxygen referred to into a more intimate state of combination, possibly with the loss of a portion of combined heat, and gives the class of monobasic metaphosphates. The general formula of a metaphosphate is—



A pyrophosphate, or so-called bibasic phosphate, is, on this view, a compound of a common phosphate and metaphosphate:—



Hence the equivalent of a pyrophosphate contains four equivalents of base and two of phosphoric acid—the reason why so many double pyrophosphates appear to exist.

Phosphoric acid is thus supposed to resemble those conjugate organic acids which combine with two equivalents of base, because they possess the elements of two different acids.

Since the existence of simple relations between the combining volumes of gaseous bodies was ascertained by Gay-Lussac, various

attempts have been made to establish similar relations between the measures, as well as the weights, in which bodies, in the liquid and solid form, enter into combination. If the atoms of all elements had, in the solid form, the same bulk, their specific gravities would be regulated by their atomic weights, and be in the same proportion. It was early observed by M. Dumas, that a close approximation to this simple ratio holds among the specific gravities of a considerable number of isomorphous bodies; but it is by no means general. The subject has received its fullest investigation from Professor Schroeder of Mannheim,\* Dr. Hermann Kopp† of Giessen, and Messrs. Playfair and Joule.‡ Much information has been collected, and many curious relations in the specific gravities of particular bodies pointed out; but the general deductions drawn can, in general, claim only a certain degree of probability. Much of the uncertainty arises from the specific gravity of a body in the solid form being often variable between rather wide limits. Thus platinum, in a pulverulent state, reduced from its oxide and from the double chloride of platinum and ammonium respectively, is found to have the specific gravity 17·766 in the first case, and 21·206 in the second, (Playfair and Joule); and the effect of compression upon the malleable metals is generally very sensible. As the rate of dilatation of different solids and liquids by heat is very dissimilar, it is obvious their relations in density may also be disturbed or disguised by temperature.

At present, I shall confine myself to a summary of the results of M. Kopp on this subject, which partake least of a speculative character. The *atomic volume*, which I substitute for the *specific volume* of Dr. Kopp, in the following tables, is the volume or measure of an equivalent or atomic proportion of the different substances enumerated. The *calculated density* is obtained by dividing the atomic weight by this volume. Thus an equivalent of mercury, 1266 parts by weight, has the volume 93 assigned to it. Now 1266, divided by 93, gives 13·6 as the “calculated” specific gravity, which coincides with the specific gravity of mercury actually observed

\* Die Molecularvolume der chemischen Verbindungen im festen und flussigen Zustande : Mannheim, 1843.

† Bemerkungen zur Volumtheorie, Braunschweig, 1844; Annales de Chimie et de Physique, 2e Sér. T. lxxv. and 3e Sér. T. iv. p. 462.

‡ Memoirs of the Chemical Society of London, vol. ii. p. 401; vol. iii. pp. 57 and 199. Also, a paper on the Constitution of Aqueous Solutions of Acids and Alkalies, by Mr. J. J. Griffin; *ibid.* p. 155.



by Kupffer and others. The atomic volume for oxygen will afterwards appear to be 16, or a multiple of that number, and is the modulus of the scale.

TABLE I.

*Atomic Volume and Specific Gravity of Elements.*

Substances.		Atomic Weight.	Primitive Atomic Volume.	Calculated Sp. Grav.	Observed Specific Gravity.
Antimony ...	Sb	806	120	6.72	6.70 Karsten; 6.6 Breithaupt; 6.85 Muschenbroeck.
Arsenic .....	As	470	80	5.87	5.70, 5.96 Guibourt; 5.62 Karsten; 5.67 Herapath.
Bismuth ...	Bi	1330	135	9.85	9.88 Thenard; 2.83 Herapath; 9.65 Karsten.
Bromine ...	Br	489	160	3.06	2.99 Loewig; 2.97 Balard.
Cadmium ...	Cd	697	81	8.60	8.66 Herapath; 8.63 Karsten, Kopp; 8.60 Stromeyer.
Chlorine ...	Cl	221	160	1.38	1.33 Faraday.
Chromium ...	Cr	352	69	5.10	5.10 Thomson.
Cobalt .....	Co	369	44	8.39	8.49 Brunner; 8.51 Berz.; 8.71 Lampadius.
Copper .....	Cu	396	44	9.00	8.96 Berzelius; 9.00 Muschenb.; 8.72 Karsten.
Cyanogen ...	Cy	165	160	1.03	About 0.9 Faraday.
Gold .....	Au	1243	65	19.1	19.26 Brisson.
Iridium .....	Ir	1233	57	21.6	19.5 Mohs; 23.5 Breithaupt.
Iodine .....	I	789	160	4.93	4.95 Gay-Lussac.
Iron .....	Fe	339	44	7.70	7.6, 7.8 Broling; 7.79 Karsten.
Lead .....	Pb	1294	114	11.35	11.33 Kupffer; 11.39 Karsten; 11.35 Herapath.
Manganese..	Mn	346	44	7.86	8.03 Bachmann; 8.01 John.
Mercury ...	Hg	1266	93	13.6	13.6 Kupffer, Karsten, Cavallo.
Molybdenum	Mo	599	69	8.68	8.62, 8.64 Bucholz.
Nickel .....	Ni	370	44	8.41	8.40 Tourte; 8.38 Tupputi; 8.60 Brunner.
Osmium ...	Os	1244	57	21.8	Native; 19.5 (?) Thenard.
Palladium ...	Pd	666	57	11.7	11.3 Wollaston; 12.1 Lowry.
Phosphorus.	P	196	111	1.77	1.77 Berzelius.
Platinum ...	Pt	1233	57	21.6	21.0 Borda; 21.5 Berzelius; 23.5 (?) Cloud.
Potassium ...	K	490	583	0.84	0.86 Gay-Lussac, Thenard; 0.87 Sementini.
Rhodium ...	R	651	57	11.4	11.0 Wollaston; 11.2 Cloud.
Selenium ...	Se	495	115	4.30	4.30, 4.32 Berzelius; 4.31 Boullay.
Silver .....	Ag	1352	130	10.4	10.4 Karsten.
Sodium .....	Na	291	292	0.99	0.97 Gay-Lussac and Thenard.
Sulphur ...	S	201	101	1.99	1.99, 2.05 Karsten; 1.99 Breithaupt.
Tin .....	St	735	101	7.28	7.28 Herapath; 7.29 Kupffer, Karsten.
Titanium ...	T	304	57	5.33	5.3 Wollaston; 5.28 Karsten.
Tungsten ...	W	1183	69	17.1	17.2 Allan and Aiken; 17.4 Bucholz.
Zinc .....	Zn	403	58	6.95	6.92 Karsten; 6.86, 7.21 Berzelius.

It will be observed that certain analogous substances possess the same atomic volume:—bromine, chlorine, cyanogen, and iodine;

chromium, molybdenum, and tungsten; cobalt, copper, iron, manganese, and nickel; iridium, osmium, palladium, platinum, and rhodium.

There are also analogous substances of which the atomic volume of one is double that of the other. The volume of an equivalent of silver is double that of gold, and the volume of potassium double that of sodium. <sup>292</sup> <sup>583</sup>

When a substance enters into combination, it either occupies its own volume, or assumes a new volume, which last may remain constant through a class of compounds. Hence the volumes in the preceding table are described as the primitive atomic volumes. The metals enumerated possess the following atomic volumes in their salts:—

	Atomic Volume in Salts.
Ammonium . . . . .	218
Barium . . . . .	143
Calcium . . . . .	60
Magnesium . . . . .	40
Potassium . . . . .	234
Sodium . . . . .	130
Strontium . . . . .	108

The other metals are supposed to retain their primitive volumes in combination.

In explaining the atomic volume of carbonates, it is supposed by Dr. Kopp that the salt-radical  $\text{CO}_3$  enters into its combinations with the atomic volume 151.

In the nitrates, the salt-radical  $\text{NO}_3$  is supposed to have the atomic volume 358.

In one class of sulphates,  $\text{SO}_4$  is supposed to have the atomic volume 236; in another, the atomic volume 186.

In the chromates, the atomic volume of  $\text{CrO}_4$  is 228; and, in the tungstates, that of  $\text{WO}_4$  is 244.

The atomic volume of chlorine is 196 in one class of chlorides, and 245 in another.

On combining the atomic volumes of the metals contained in the salts with these suppositions for their salt-radicals, the atomic volume of the compound is obtained, and the following calculated specific gravities:—

TABLE II.

*Atomic Volume and Specific Gravity of Salts.*

## CARBONATES.

CARBONATES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp.Gr.	Observed Specific Gravity.
Cadmium.....	1073	$\text{Cd} + \text{CO}_3$	$81 + 151 = 232$	4.63	4.42 Herapath; 4.49 K.
Iron.....	715	$\text{Fe} + \text{CO}_3$	$144 + 151 = 195$	3.67	3.83 Mohs; 3.87 Naumann.
Lead .....	1670	$\text{Pb} + \text{CO}_3$	$114 + 151 = 265$	6.30	6.43 Karsten; 6.47 Breithaupt.
Manganese ...	722	$\text{Mn} + \text{CO}_3$	$44 + 151 = 195$	3.70	3.55, 3.59 Mohs.
Silver .....	1728	$\text{Ag} + \text{CO}_3$	$130 + 151 = 281$	6.15	6.08 Karsten.
Zinc.....	779	$\text{Zn} + \text{CO}_3$	$58 + 151 = 209$	3.73	4.44 Mohs; 4.4, 4.5 Naumann.
Baryta.....	1233	$\text{Ba} + \text{CO}_3$	$143 + 151 = 294$	4.19	4.30 Karsten; 4.24 Breithaupt; 4.30 Mohs.
Lime .....	632	$\text{Ca} + \text{CO}_3$	$60 + 151 = 211$	3.00	<div style="display: inline-block; vertical-align: middle;">           Arragonite 3.00            Breithaupt; 2.93 Mohs.            Calc. spar 2.70            Karsten; 2.72 Beudant.         </div>
Magnesia.....	534	$\text{Mg} + \text{CO}_3$	$40 + 151 = 191$	2.80	2.81 Breithaupt; 3.00, 3.11 Mohs; 2.88, 2.97 Naum.
Potash.....	866	$\text{K} + \text{CO}_3$	$234 + 151 = 385$	2.25	2.26 Karsten.
Soda .....	667	$\text{Na} + \text{CO}_3$	$130 + 151 = 281$	2.37	2.47 Karsten.
Strontia .....	923	$\text{Sr} + \text{CO}_3$	$108 + 151 = 259$	3.56	3.60 Mohs; 3.62 K.
Dolomite.....	1166	$\left\{ \begin{array}{l} \text{Mg} + \text{CO}_3 \\ \text{Ca} + \text{CO}_3 \end{array} \right.$	$\left\{ \begin{array}{l} 40 + 151 \\ 60 + 151 \end{array} \right. = 402$	2.90	2.88 Mohs.
Mesiline .....	1250	$\left\{ \begin{array}{l} \text{Mg} + \text{CO}_3 \\ \text{Fe} + \text{CO}_3 \end{array} \right.$	$\left\{ \begin{array}{l} 40 + 151 \\ 44 + 151 \end{array} \right. = 386$	3.24	3.35 Mohs.

## NITRATES.

NITRATES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp.Gr.	Observed Specific Gravity.
Lead .....	2071	$\text{Pb} + \text{NO}_3$	$114 + 358 = 472$	4.40	4.40 Karsten; 4.77 Breithaupt; 4.34 Kopp.
Silver.....	2129	$\text{Ag} + \text{NO}_3$	$130 + 358 = 488$	4.36	4.36 Karsten.
Ammonia ...	1004	$\text{Am} + \text{NO}_3$	$218 + 358 = 576$	1.74	1.74 Kopp.
Baryta .....	1634	$\text{Ba} + \text{NO}_3$	$143 + 358 = 501$	3.20	3.19 Karsten.
Potash .....	1267	$\text{K} + \text{NO}_3$	$234 + 358 = 592$	2.14	2.10 Karst.; 2.06 Kopp.
Soda .....	1068	$\text{Na} + \text{NO}_3$	$130 + 358 = 488$	2.19	2.19 Marx; 2.20 Kopp; 2.26 Karsten.
Strontia .....	1324	$\text{Sr} + \text{NO}_3$	$108 + 358 = 466$	2.84	2.89 Karsten.

## SULPHATES: FIRST CLASS.

SULPHATES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp.Gr.	Observed Specific Gravity.
Copper .....	997	Cu + SO <sub>4</sub>	44 + 236 = 280	3·56	3·53 Karsten.
Silver .....	1953	Ag + SO <sub>4</sub>	130 + 236 = 366	5·34	5·34 Karsten.
Zinc.....	1004	Zn + SO <sub>4</sub>	58 + 236 = 294	3·42	3·40 Karsten.
Lime .....	857	Ca + SO <sub>4</sub>	60 + 236 = 296	2·90	2·96 Naumann; 2·93 Karsten.
Magnesia.....	759	Mg + SO <sub>4</sub>	40 + 236 = 276	2·75	2·61 Karsten.
Soda .....	892	Na + SO <sub>4</sub>	130 + 236 = 366	2·44	2·46 Mohs; 2·63 K.

## SULPHATES: SECOND CLASS.

SULPHATES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp.Gr.	Observed Specific Gravity.
Lead .....	1895	Pb + SO <sub>4</sub>	114 + 186 = 300	6·32	6·30 Mohs; 6·17 Karst.
Baryta.....	1458	Ba + SO <sub>4</sub>	143 + 186 = 329	4·43	4·45 Mohs; 4·20 Karst.
Potash.....	1091	K + SO <sub>4</sub>	234 + 186 = 420	2·60	2·62 Karst.; 2·66 Kopp.
Strontia .....	1148	Sr + SO <sub>4</sub>	108 + 186 = 294	3·90	3·95 Breithaupt; 3·59 Karsten.

## CHROMATES AND TUNGSTATES.

CHROMATES and TUNGSTATES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp.Gr.	Observed Specific Gravity.
Lead .....	2046	Pb + CrO <sub>4</sub>	114 + 228 = 342	5·98	5·95 Breithaupt; 6·00 Mohs.
Potash.....	1241	K + CrO <sub>4</sub>	234 + 228 = 462	2·69	2·64 Karst.; 2·70 Kopp.
Lead .....	2877	Pb + WO <sub>4</sub>	114 + 244 = 358	8·04	8·0 Gmel.; 8·1 Leonh.
Lime .....	1839	Ca + WO <sub>4</sub>	60 + 244 = 304	6·05	6·04 Kars.; 6·03 Meiss.

## CHLORIDES: FIRST CLASS.

CHLORIDES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp.Gr.	Observed Specific Gravity.
Lead .....	1736	Pb + Cl	114 + 196 = 310	5·60	5·68, 5·80 Karsten;
Silver .....	1794	Ag + Cl	130 + 196 = 326	5·50	5·24, 5·34 Monro.
Barium .....	1299	Ba + Cl	143 + 196 = 339	3·83	5·50, 5·57 Kars.; 5·55 Boul.; 5·13 Herap.
Sodium .....	733	Na + Cl	130 + 196 = 326	2·25	3·86 Boul.; 3·70 Kars.
					2·26 Mohs; 2·15 Kopp;
					2·08 Karsten.



## CHLORIDES: SECOND CLASS.

CHLORIDES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp.Gr.	Observed Specific Gravity.
Copper .....	1234	2Cu + Cl	$88 + 245 = 333$	3.70	3.68 Karsten.
	1708	Hg + Cl	$93 + 245 = 338$	5.05	5.14 Gmel.; 5.43 Boul.; 5.40 Karsten.
Mercury ...	2974	2Hg + Cl	$186 + 245 = 431$	6.90	6.99 Karst.; 6.71 Herapath; 7.14 Boul.
Ammonium...					1.45 Watson; 1.50 Kopp; 1.53 Mohs.
Calcium .....	698	Ca + Cl	$60 + 245 = 305$	2.29	2.21, 2.27 Boul.; 1.92 Karsten.
Potassium ...	932	R + Cl	$234 + 245 = 479$	1.94	1.94 Kopp; 1.92 Karst.
Strontium ...	989	Sn + Cl	$108 + 245 = 353$	2.80	2.80 Karsten.

In explaining the specific gravity of oxides, it is necessary to make three assumptions for the specific volume of oxygen. In the first small class of oxides, the oxygen is contained with the atomic volume 16; in the second and large class, with the atomic volume 32; and, in the third class, with the atomic volume 64. The metals are supposed to retain their primitive atomic volumes.

TABLE III.

*Atomic Volume and Specific Gravity of Oxides.*

## FIRST CLASS.

OXIDES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp.Gr.	Observed Specific Gravity.
Antimony ...	1006	Sb + 2O	$120 + 32 = 154$	6.53	6.53 Boullay; 6.70 Karst.
Chromium ...	1003	2Cr + 3O	$138 + 48 = 186$	5.39	5.21 Wöhler.
Tin.....	935	Sn + 2O	$101 + 32 = 133$	7.03	6.96 Mohs; 6.90 Boullay; 6.64 Herapath.

## SECOND CLASS.

OXIDES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp.Gr.	Observed Specific Gravity.
Antimony ...	1913	2Sb + 3O	240 + 96 = 336	5·69	5·78 Boullay; 5·57 Mohs.
Bismuth .....	2960	2Bi + 3O	270 + 96 = 366	8·09	8·17 Karst.; 8·21 Herap.; 8·45 Royer and Dum.
Cadmium ...	797	Cd + O	81 + 32 = 113	7·05	6·95 Karsten.
Cobalt .....	1038	2Co + 3O	88 + 96 = 184	5·64	5·60 Boullay; 5·32 Herap.
Copper .....	496	Cu + O	44 + 32 = 76	6·53	6·43 Karst.; 6·13 Boul.; 6·40 Herapath.
Iron .....	978	2Fe + 3O	88 + 96 = 184	5·31	5·23 Boullay; 5·25 Mohs.
	1394	Pb + O	114 + 32 = 146	9·55	9·50 Boullay; 9·28 Herap. 9·21 Karsten.
Lead .....	1494	Pb + 2O	114 + 64 = 178	8·40	8·90 Herap.; 8·92 Karst.
	2889	2Pb + 3O	228 + 96 = 324	8·91	8·94 Muschenbroek; 8·60 Karst.; 9·20 Boullay.
Manganese...	446	Mn + O	44 + 32 = 76	5·87	4·73 Herapath.
Mercury .....	1366	Hg + O	98 + 32 = 125	10·9	11·0 Boullay; 11·1 Herapath; 11·2 Karsten.
Molybdenum.	799	Mo + 2O	69 + 64 = 133	6·01	5·67 Bucholz.
Tin .....	885	Sn + O	101 + 32 = 133	6·28	6·67 Herapath.
Titanium ...	504	Ti + 2O	57 + 64 = 121	4·16	4·18 Klaproth; 4·20, 4·25 Breithaupt.
Zinc .....	503	Zn + O	58 + 32 = 90	5·48	5·43 Mohs; 5·60 Boullay; 5·73 Karsten.
Ilmenite .....	942	$\left\{ \begin{smallmatrix} \text{Fe} \\ \text{Ti} \end{smallmatrix} \right\} + 3\text{O}$	$\left\{ \begin{smallmatrix} 44 \\ 57 \end{smallmatrix} \right\} + 96 = 197$	4·78	4·73, 4·79 Breithaupt; 4·75, 4·78 Kupffer.

## THIRD CLASS.

OXIDES.	Atomic Weight.	Formula.	Calculated Atomic Volume.	Calculated Sp.Gr.	Observed Specific Gravity.
Copper .....	892	2Cu + O	88 + 64 = 152	5·87	5·75 Karsten, Royer and Dumas; 6·05 Herapath.
Mercury .....	2632	2Hg + O	186 + 64 = 250	10·05	10·69 Herap.; 8·95 Karst.
Molybdenum.	899	Mo + 3O	69 + 192 = 261	3·44	3·46 Bergman, Thomson; 3·49 Berzelius.
Silver .....	1452	Ag + O	88 + 64 = 152	7·48	7·14 Herapath; 7·25 Boullay; 8·26 Karsten.
Tungsten ...	1483	W + 3O	69 + 192 = 261	5·68	5·27 Herapath; 6·12 Berzelius; 7·14 Karsten.

Dr. Kopp has endeavoured to determine the atomic volume of the constituents of many other classes of compounds. The specific gravity of the compounds of sulphur and arsenic with the metals, of water with oxides and salts, of chlorine with the non-metallic elements, are explained in a similar manner on a small number of suppositions. He also shows with considerable success that in those isomorphous

substances, of which the crystalline form is only similar, and not absolutely identical, as the carbonates (p. 162), the observed difference between the atomic volumes corresponds with the difference between the crystalline forms. The variation in the atomic volume is thus manifested by a variation in the crystalline form.

Revised in 1850, adding Feb. 6

## CHAPTER IV.

### CHEMICAL AFFINITY.

IN the preceding section, compound bodies have been viewed as already formed, and existing in a state of rest. The arrangement, weights, and other properties of their atoms, have also been examined with the relations and classification of the compounds themselves. But chemistry is more than a descriptive science; for it embraces, in addition to views of composition, the consideration of the action of bodies upon each other, which leads to the formation and destruction of compounds. Certain bodies, when placed in contact, exhibit a proneness to combine with each other, or to undergo decomposition, while others may be mixed most intimately without change. The actual phenomena of combination suggest the idea of peculiar attachments and aversions subsisting between different bodies, and it was in this figurative sense that the term *affinity* was first applied by Boerhaave to a property of matter. A specific attraction between different kinds of matter must be admitted as the cause of combination, and this attraction may be conveniently distinguished as *chemical affinity*.

The particles of a body in the solid or liquid state exhibit an attraction for each other, which is the force of *cohesion*, and even different kinds of matter have often an attraction for each other, which is probably of the same nature, although distinguished as *adhesion*. This force retains bodies in contact which are once placed in sufficient proximity to each other. It is exhibited in the adhesion of two smooth pieces of lead pressed together, or perfectly flat pieces of plate-glass, which sometimes cannot again be separated. The action of glue, wax, mortar, and other cements, in attaching bodies

together, depends entirely upon the same force. In detaching glue from the surface of glass, the latter is sometimes injured, and portions of it are torn off by the glue, the adhesive attraction of the two bodies being greater than the cohesion of the glass. The property of water to adhere to solid surfaces and wet them, its imbibition by a sponge, the ascent of liquids in narrow tubes, and other phenomena of capillary attraction, and the rapid diffusion of a drop of oil over the surface of water, are illustrations of the same attraction between a liquid and a solid, and between different liquids. But this kind of attraction is deficient in a character which is never absent in true chemical affinity—*it effects no change in the properties of bodies*. It may bind different kinds of matter together, but it does not alter their nature.

Jan. 31, 1849

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Diffusion  
of liquids & gases  
1840.

The tendency of different gases to diffuse through each other till a uniform mixture is formed, is another property of matter,—the effect of a force wholly independent of chemical affinity. It is certain that this physical property is not lost in liquids, and that it contributes to that equable diffusion of a salt through a menstruum which occurs spontaneously, and without agitation to promote it.\*

*Solution.*—The attraction between salt and water, which occasions the solution of the former, differs in several circumstances from the affinity which leads to the production of definite chemical compounds. In solution, combination takes place in indefinite proportions, a certain quantity of common salt dissolving in, or combining with any quantity of water however large; while a certain quantity of water, such as 100 parts, can dissolve any quantity of that salt less than 37 parts, the proportion which saturates it. Water has a constant solvent power for every other soluble salt; but the maximum proportion of salt dissolved, or the saturating quantity, has no relation to the atomic weight of the salt, and indeed varies exceedingly with the temperature of the solvent. The limit to the solubility of a salt seems to be immediately occasioned by its cohesion. Water, in proportion as it takes up salt, has its power to disintegrate and dissolve more of the soluble body gradually diminished; it dissolves the last portions slowly and with difficulty, and at last, when saturated, is incapable of overcoming the cohesion of more salt that may be added to it. The solubility in water of another body in the liquid

\* Jerichau, in Poggendorff's *Annalen*, xxxiv. 613; or Dove and Moser's *Repertorium der Physik*, i. 96, 1837.



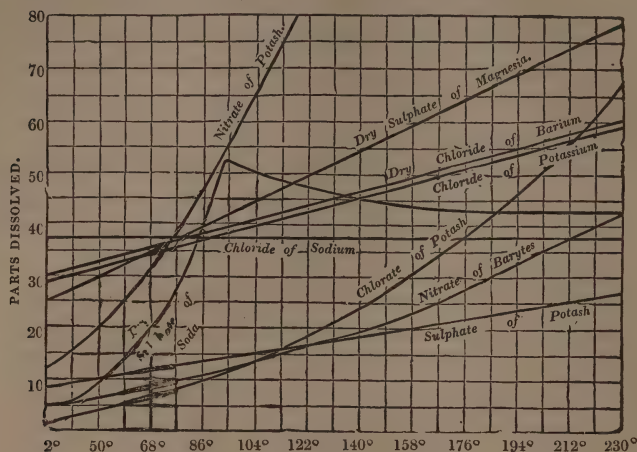
state is not restrained by cohesion, and is in general unlimited. Thus alcohol, and also soluble salts above the temperature at which they liquefy in their water of crystallization, dissolve in water in any proportion. Generally speaking, also, those salts dissolve in largest quantity which are most fusible, or of which the cohesion is most easily overcome by heat, as the hydrated salts; and among anhydrous salts, the nitrates, chlorates, chlorides, and iodides, which are all remarkable for their fusibility. In this species of combination, bodies are not materially altered in properties; indeed, are little affected except in their cohesion.

The union also between a body and its solvent differs in a marked manner from proper chemical combination in the relation of the bodies to each other which exhibit it. Bodies *combine* chemically with so much the more force as their properties are more opposed, but they *dissolve* the more readily in each other, the more similar their properties. Thus, metals combine with non-metallic bodies, acids with alkalies; but to dissolve a metal, another metal must be used, such as mercury; oxidated bodies dissolve in oxidated solvents, as the salts and acids in water; while liquids which contain much hydrogen are the best solvents of hydrogenated bodies—an oil, for instance, of a fat or a resin; alcohol and ether dissolving the essential oils and most organic principles, but few salts of oxygen acids. The force which produces solution differs, therefore, essentially from chemical affinity in being exerted between analogous particles, in preference to particles which are very unlike; and resembles more, in this respect, the attraction of cohesion.

A more accurate idea of the varying solubility of a salt at different temperatures may be conveyed by a curve constructed to represent it, than by any other means. The perpendicular lines in the following diagram, indicate the degrees of temperature which are marked below them, and the horizontal lines, quantities of salt dissolved by 100 parts by weight of water. The proportion of any salt dissolved at a particular temperature may be learned by carrying the eye along the perpendicular line expressing that temperature, till it cuts the curve of the salt, and then horizontally to the column of parts dissolved.\*

\* An extensive and very careful series of experiments on the solubility of salts in water at different temperatures has been made by M. Poggiale, Ann. de Chim. et de Phys. 3e Sér. T. viii. p. 463; and the *Rapport Annuel* of Berzelius, Paris, 1846, p. 18.

## SOLUBILITY OF SALTS IN ONE HUNDRED PARTS OF WATER.



It will be observed that the perpendicular lines advance by  $9^\circ$ , the first being  $32^\circ$ , and the last  $230^\circ$ . The solubility of nitrate of potash increases from 13 parts in 100 water at  $32^\circ$ , to 80 parts at  $118^\circ$ , or very rapidly with the temperature. Sulphate of soda is seen by the form of its curve to increase in solubility from 5 parts at  $32^\circ$  to 52 parts at  $92^\circ$ , but then to diminish in solubility with farther elevation of temperature. In this salt, sulphate of magnesia and chloride of barium, the solubility is expressed in parts of the anhydrous, and not the hydrated salt. The lines of chloride of barium and chloride of potassium are parallel, shewing a remarkable relation between the solubilities of these two salts, which does not appear in any others. The line of chloride of sodium is observed to cut all the lines of temperature at the same height, 100 parts of water dissolving 37 parts of that salt at all temperatures.

*Intensity of solubility*  
*Boiling point*  
*2. Difficult to*  
 Chemical affinity acts only at insensible distances, and has no effect in causing bodies to approach each other which are not in contact, differing in this respect from the attraction of gravitation, which acts at all distances, however great, although with a diminishing force. Hence, the closest approximation of unlike particles is necessary to develop their affinities, and produce combination. Sulphur and copper in mass have no effect upon each other, but if both be in a state of great division, and rubbed together in a mortar, a powerful affinity is brought into play, the bodies themselves disappear, and sulphuret of copper is produced by their union, with the evolution of much heat. The affinity of bodies is, therefore, promoted by every

thing which tends to their close approximation; in solids, by their pulverization and intermixture, this attraction residing in the ultimate particles of bodies; in gases, by their spontaneous diffusion through each other, which occasions a more complete intermixture than is attainable by mechanical means; and between liquids, or between a liquid and solid, by the adhesive attraction which liquids possess, which must lead to perfect contact, and also by a disposition of liquid bodies to intermix, of the same physical character as gaseous diffusion. Elevation of temperature has certainly often a specific action in increasing the affinity of two bodies, but it also often acts by producing a perfect contact between them, from the fusion or vaporization of one or both bodies. Hence, no practice is more general to promote the combination of bodies than to heat them together.

If the affinity between two gases is sufficiently great to begin combination, the process is never interrupted, but is continued from the diffusion of the gases through each other till complete, or at least till one of the gases is entirely consumed. Thus, when hydrochloric acid and ammoniacal gases, in equal measures, are introduced into a jar containing at the same time a large quantity of air, the formation of hydrochlorate of ammonia proceeds, the gases appearing to search out each other, till no portion of uncombined gas remains. The combination of two liquids, or of a liquid and a solid, is also facilitated in the same manner by the mobility of the fluid, and proceeds without interruption, unless, perhaps, the product of the combination be solid, and by its formation interpose an obstacle to the contact of the combining bodies. But the affinities of two solids which are not volatile are rarely developed at all, owing to the imperfection of contact. Even the action of very powerful affinities between a solid and a liquid or a gas, is often arrested in the outset from the physical condition of the former. Thus, the affinity between oxygen and lead is certainly considerable, for the metal is rapidly converted into a white oxide when ground to powder and agitated with water in its usual aerated condition; and in the state of extreme division in which lead is obtained by calcining its tartrate in a glass tube, the metal is a pyrophorus, and combines with oxygen when cold with so much avidity as to take fire and burn the moment it is exposed to the air. Iron also, in the spongy and divided state in which it is procured, by reducing the peroxide by means of hydrogen gas at a low red heat, absorbs oxygen with equal avidity at the temperature of the air, and takes fire and burns. But notwithstanding an affinity for oxygen of such intensity, these metals in mass oxidate very slowly in air, parti-

*Feb. 1. 1848*  
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cularly lead, which is quickly tarnished indeed, but the thin coating of oxide formed does not penetrate to a sensible depth in the course of several years. The suspension of the oxidation may be partly due to the comparatively small surface which a compact body exposes to air, and which becomes covered by a coat of oxide, and protected from farther change; but partly also to the effect of the conducting power of a considerable mass of metal in preventing the elevation of temperature consequent upon the oxidation of its surface. For metals oxidate with increased facility at a high temperature, such as the lead pyrophorus quickly attains from the oxidation of the great surface which it exposes, compared with its weight. The heat from the oxidation of the superficial particles of the compact metal, however, is not accumulated, but carried off and dissipated by the conducting power of the contiguous particles, so that elevation of temperature is effectually repressed. It thus appears that the state of aggregation of a solid may oppose an insuperable bar to the action of a very powerful affinity.

*Quick O<sup>c</sup> from  
Cult. in Hydrog.* The affinity of two bodies, one or both of which are in the state of gas, is often promoted in an extraordinary manner by the contact of certain solid bodies. Thus, oxygen and hydrogen gases may be mixed and retained for any length of time in that state without exhibiting any affinity for each other, and the gaseous mixture may, indeed, be heated in a glass vessel to any temperature short of redness without showing any disposition to combine. But if a clean plate of platinum be introduced into the cold mixture, the gases in contact with the metallic surface instantly unite and form water; other portions of the mixture come then in contact with the platinum, and combine successively under its influence, so that a large quantity of the gaseous mixture may be quickly united. The temperature of the platinum also rises, from the heat evolved by the combination occurring at its surface, and the influence of the metal increasing with its temperature, combination proceeds at an accelerated rate, till the platinum becoming red hot, may cause the combination to extend to a distance from it, by kindling the gaseous mixture. Platinum acts in this manner with greatest energy when in a highly divided state, as in the form of spongy platinum, owing to the greater surface exposed, and the rapidity with which it is heated. The metal itself contributes no element to the water formed, and is in no respect altered. It is an action of the metallic surface, which must be perfectly clean, and is retarded or altogether prevented by the presence of oily vapours and many other combustible gases, which soil the metallic surface.



Mr. Faraday is disposed to refer the action to an adhesive attraction of the gases for the metal, under the influence of which they are condensed and their particles approximated within the sphere of their mutual attraction, so as to combine. This opinion is favoured by the circumstance that the property is not peculiar to platinum, but appears also in other metals, in charcoal, pounded glass, and all other solid bodies; although all of them, except the metals, act only when their temperature is above the boiling point of mercury. But, on the other hand, at low temperatures, the property appears to be confined to a few metals only which resemble platinum in their chemical characters; namely, in having little or no disposition to combine with oxygen gas, and in not undergoing oxidation in the air. The action of platinum may, therefore, be connected with its chemical properties, although in a way which is quite unknown to us. The same metal disposes carbonic oxide gas to combine with oxygen, but much more slowly than hydrogen; and it is remarkable that if the most minute quantity of carbonic oxide be mixed with hydrogen, the oxidation of the latter under the influence of the platinum is arrested, and not resumed till after the carbonic oxide has been slowly oxidated and consumed, which thus takes the precedence of the hydrogen in combining with oxygen. This extraordinary interference of a minute quantity of carbonic oxide gas, which cannot from its nature be supposed to soil the surface of the platinum like a liquefiable vapour, seems to point to a chemical, perhaps to an electrical explanation of the action of the platinum, rather than to the adhesive attraction of the metal. The oxidation of alcohol <sup>with in the liquid or vapourous condition</sup> at the temperature of the air, and also at a low red heat, is promoted in the same manner by contact with platinum.

Jan. 28, 1850  
slow

*Order of affinity.*—The affinity between bodies appears to be of different degrees of intensity. Lead, for instance, has certainly a greater affinity than silver for oxygen, the oxide of the latter being easily decomposed when heated to redness, while the oxide of the former may be exposed to the most intense heat without losing a particle of oxygen. Again, it may be inferred that potassium has a still greater affinity for oxygen than lead possesses, as we find the oxide of lead easily reduced to the metallic state when heated in contact with charcoal, while potash is decomposed in the same manner with great difficulty. But the order of affinity is often more strikingly exhibited in the decomposition of a compound by another body. Thus, sulphuretted hydrogen gas is decomposed by iodine, which combines with the hydrogen, forming hydriodic acid, and liberates

sulphur. The affinity of iodine for hydrogen is, therefore, greater than that of sulphur for the same body. But hydriodic acid is deprived of its hydrogen by bromine, and hydrobromic acid is formed; and this last is decomposed in its turn by chlorine, and hydrochloric acid produced. It thus appears that the order of the affinity of the elements mentioned *for hydrogen* is, chlorine, bromine, iodine, sulphur. The order of decompositions, in the precipitation of metals by each other from their saline solutions, also indicates the degree of affinity. Thus, from the decomposition of the nitrates of the following metals, the order of their affinity *for nitric acid and oxygen* may be inferred to be as follows:—zinc, lead, copper, mercury, silver; zinc throwing down lead from the nitrate of lead, and all the other metals which follow it; lead throwing down copper; copper, mercury; and mercury, silver; while nitrate of zinc itself is not affected by any other metal, and nitrate of silver is decomposed by all the metals enumerated. Bodies were first thus arranged according to the degree of their affinity for a particular substance, inferred from the order of their decompositions, by Geoffroy and Bergman, and tables of affinity constructed, of which the following is an example:—

*Order of Affinity of the Alkalies and Earths for Sulphuric Acid.*

Baryta.  
Strontia.  
Potash.  
Soda.  
Lime.  
Ammonia.  
Magnesia.

Baryta is capable of taking sulphuric acid from strontia, potash, and every other base which follows it in the table,—the experiment being made upon sulphates of these bases dissolved in water; while sulphate of baryta is not decomposed by any other base. Lime separates ammonia and magnesia from sulphuric acid, but has no effect upon the sulphates of soda, potash, strontia, and baryta; and in the same manner any other base decomposes the sulphates of the bases below it in the column, but has no effect upon those above it. Tables of this kind, when accurately constructed, may convey much valuable information of a practical kind, but it is never to be forgotten that they are strictly tables of the order of decomposition and of the comparative force or order of affinity in one set of conditions only. This will appear by examining how far decomposition is affected by accessory circumstances in a few cases.

*Circumstances which affect the order of decomposition.*—Volatility in a body promotes its separation from others which are more fixed, and consequently facilitates the decomposition of compounds into which the volatile body enters. Hence, by the agency of heat, water is separated from hydrated salts; ammonia, from its combinations with a fixed acid, such as the phosphoric; and a volatile acid from many of its salts: as sulphuric acid from the sulphate of iron, carbonic acid from the carbonate of lime, &c. Ammonia decomposes hydrochlorate of morphia at a low temperature, but, on the other hand, morphia decomposes the hydrochlorate of ammonia at the boiling point of water, and liberates ammonia, owing to the volatility of that body. The fixed acids, such as the silicic and phosphoric, disengage in the same way at a high temperature those acids which are generally reputed most powerful, and by which silicates and phosphates are decomposed with facility at a low temperature. Many such cases might be adduced in which the order of decomposition is reversed by a change of temperature. The volatility of one of its constituents must, therefore, be considered <sup>as</sup> an element of instability in a compound.

Decomposition from unequal volatility is, of course, checked by pressure, and promoted by its removal and by every thing which favours the escape of vapour; such as the presence of an atmosphere of a different sort into which the volatile constituent may evaporate. Carbonate of lime is decomposed easily at a red heat, provided a current of air or of steam is passing over it which may carry off the carbonic acid gas, but the decomposition ceases when the carbonate is surrounded by an atmosphere of its own gas; and the carbonate may even be heated to fusion, in the lower part of a crucible, without decomposition. Here the occurrence of decomposition depends entirely upon the existence of a foreign atmosphere into which carbonic acid can diffuse. Nitrates of alumina, and peroxide of iron in solution, are decomposed by the spontaneous evaporation of their acid, even at the temperature of the air; and so is an alkaline bicarbonate when in solution, but not when dry. <sup>any temperature above</sup> A change in the composition of the gaseous atmosphere may affect the order of decomposition, as in the following cases:—

When steam is passed over iron at a red heat, a portion of it is decomposed, oxide of iron being formed and hydrogen gas evolved. From this experiment it might be inferred that the affinity of iron for oxygen is greater than that of hydrogen. But let a stream of hydrogen gas be conducted over oxide of iron at the

*Gulf State of  
Strontian, High  
assists by H.O.*

*Inter-diagram*

very same temperature, and water is formed, while the oxide of iron is reduced to the metallic state. Here the hydrogen appears to have the greater affinity for oxygen. But the result is obviously connected with the relative proportion between the hydrogen and steam which are at once in contact with the metal and its oxide at a red heat. When steam is in excess, water is decomposed, but when hydrogen is in excess, oxide of iron is decomposed; and why? because the excess of steam in the first case is an atmosphere into which hydrogen can diffuse, and the disengagement of that gas is therefore favoured; but in the second case the atmosphere is principally hydrogen, and represses the evolution of more hydrogen, but facilitates that of steam. The affinity of iron and hydrogen for oxygen at the temperature of the experiment is so nearly balanced, that the one affinity prevails over the other, according as there is a proper atmosphere into which the gaseous product of its action may diffuse. This affords an intelligible instance of the influence of mass or quantity of material, in promoting a chemical change; the steam or the hydrogen, as it preponderates, exerting a specific influence, in the capacity of a gaseous atmosphere.

[The remarkable decomposition of alcohol by sulphuric acid, which affords ether, is another similar illustration of decomposition depending upon volatility, and affected by changes in the nature of the atmosphere into which evaporation takes place. Alcohol or the hydrate of ether is added in a gradual manner to sulphuric acid somewhat diluted, and heated to  $280^{\circ}$ . In these circumstances, the double sulphate of ether and water is formed; water, which was previously combined as a base to the acid, being displaced by ether, and set free together with the water of the alcohol. The first effect of the reaction, therefore, is the disengagement of watery vapour, and the creation of an atmosphere of that substance which tends to check its farther evolution. But the existence of such an atmosphere offers a facility for the evaporation of ether, which accordingly escapes from combination with the acid and continues to be replaced by the water, the affinity of sulphuric acid for water and for ether being nearly equal, till ether forms such a proportion of the gaseous atmosphere as to check its own evolution, and to favour the evolution of watery vapour. Then the sulphate of ether comes in its turn to be decomposed as before, and ether evolved. Hence, both ether and water distil over in this process, the evolution of one of these bodies favouring

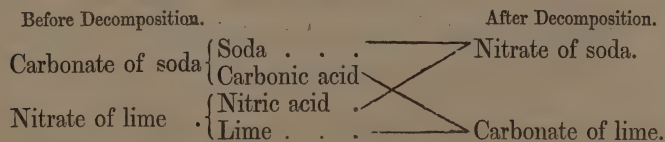


the separation and disengagement of the other. In this description, the evolution of water and ether are for the sake of perspicuity supposed to alternate, but it is evident that the result of such an action will be the simultaneous evolution of the two vapours in a certain constant relation to each other. ]

*Influence of insolubility.*—The great proportion of chemical reactions which we witness are exhibited by bodies dissolved in water or some other menstruum, and are affected to a great extent by the relations of themselves and their products to their solvent. Thus carbonate of potash dissolved in water is decomposed by acetic acid, and carbonic acid evolved, the affinity of the acetic acid prevailing over that of the carbonic acid for potash. But if a stream of carbonic acid gas be sent through acetate of potash dissolved in alcohol, acetic acid is displaced, or the carbonic acid prevails, apparently from the insolubility of the carbonate of potash in alcohol. The insolubility of a body appears to depend upon the cohesive attraction of its particles, and such decompositions may therefore be ascribed to the prevalence of that force.

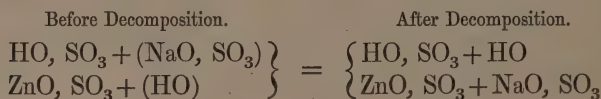
*Formation of compounds by substitution.*—It is remarkable that compounds are in general more easily formed by substitution, than by the direct union of their constituents; indeed, many compounds can be formed only in that manner. Carbonic acid is not absorbed by anhydrous lime, but readily by the hydrate of lime, the water of which is displaced in the formation of the carbonate. In the same manner, ether, although a strong base, does not combine directly with acids, but the salts of ether are derived from its hydrate or alcohol, by the substitution of an acid for the water of the alcohol. In all the cases, likewise, in which hydrogen is evolved during the solution of a metal in a hydrated acid, a simple substitution of the metal for hydrogen occurs.

Combination takes place with the greatest facility of all when *double decomposition* can occur. Thus carbonate of lime is instantly formed and precipitated, when carbonate of soda is added to nitrate of lime, nitrate of soda being formed at the same time and remaining in solution.



*Draps.*

Here a double substitution occurs, lime being substituted for soda in the carbonate, and soda for lime in the nitrate. Such reactions may therefore be truly described as double substitutions as well as double decompositions. They are most commonly observed on mixing two binary compounds or two salts. But reactions of the same nature may occur between compounds of a higher order, such as double salts, and new compounds be thus produced, which cannot be formed by the direct union of their constituents. Thus the two salts, sulphate of zinc and sulphate of soda, when simply dissolved together, at the ordinary temperature, always crystallize apart, and do not combine. But the double sulphate of zinc and soda is formed on mixing strong solutions of sulphate of zinc and bisulphate of soda, and separates by crystallization; the sulphate of water with constitutional water (hydrated acid of sp. gr. 1.78) being produced at the same time, and remaining in solution. The reaction which occurs may be thus expressed:



in which the constituents of both salts before decomposition inclosed in brackets, are found to have exchanged places after decomposition, without any other change in the original salts.\* The double sulphate of lime and soda can be formed artificially only in circumstances which are somewhat similar. It is produced on adding sulphate of soda to acetate of lime, the sulphate of lime, as it then precipitates, carrying down sulphate of soda in the place of constitutional water (Liebig).

Different hydrates of the same body, such as peroxide of tin, differ sensibly in properties, and afford different compounds with acids, unquestionably because these compounds are formed by substitution. The constant formation of phosphates containing one, two, or three atoms of base, on neutralising the corresponding hydrates of phosphoric acid with a fixed base, likewise illustrates in a striking manner the derivation of compounds, on this principle. Many insoluble substances, such as the earth silica, possess a larger proportion of water, when newly precipitated, than they retain afterwards, and in that high state of hydration they may exhibit affinities for certain bodies which

\* On Water as a Constituent of Sulphates, Phil. Mag. 3d series, vol. vi. p. 417.

do not appear in other circumstances. Hydrated silica dissolves in water at the moment of its separation from a caustic alkali; and alumina dissolves readily in ammonia, when produced in contact with that substance by the oxidation of aluminum. The usual disposition to enter into combination, which silica and alumina then exhibit, is generally ascribed to their being in the *nascent state*; a body at the moment of its formation and liberation, in consequence of a decomposition, being, it is supposed, in a favourable condition to enter anew into combination. But their degree of hydration in the nascent state may be the real cause of their superior aptitude to combine.

Double decompositions take place without the great evolution of heat which often accompanies the direct combination of two bodies, and with an apparent facility or absence of effort, as if the combinations were just balanced by the decompositions which occur at the same time. It is, perhaps, from this cause that the result of double decomposition is so much affected by circumstances, particularly by the insolubility of one of the compounds. For it is a general law, to which there is no exception, that two soluble salts cannot be mixed without the occurrence of decomposition, if one of the products that may be formed is an insoluble salt. On mixing carbonate of soda and nitrate of lime, the decomposition seems to be determined entirely by the insolubility of the carbonate of lime, which precipitates. When sulphate of soda and nitrate of potash are mixed, no visible change occurs, and it is doubtful whether the salts act upon each other, but if the mixed solution be concentrated, decomposition occurs, and sulphate of potash separates by crystallization owing to its inferior solubility.

It may sometimes be proved that double decomposition occurs on mixing soluble salts, although no precipitation supervenes. Thus, on mixing strong solutions of sulphate of copper and chloride of sodium, the colour of the solution changes from blue to green, which indicates the formation of chloride of copper and consequently that of sulphate of soda also. Now it is known that hydrochloric acid will displace sulphuric acid from the sulphate of copper at the temperature of the experiment, while sulphuric acid will, on the other hand, displace hydrochloric from chloride of sodium. It hence appears that in the preceding double decomposition, those acids and bases unite which have the strongest affinity for each other, and the same thing

may happen on mixing other salts. But where the order of the affinities for each other of the acids and bases is unknown, the occurrence of any change upon mixing salts, or the extent to which the change proceeds, is entirely matter of conjecture.

It was the opinion of Berthollet, founded principally upon the phenomena of the double decompositions of salts, that decompositions are at all times dependent upon accidental circumstances, such as the volatility or insolubility of the product, and never result from the prevalence of certain affinities over others; and consequently that in accounting for such changes, the consideration of affinity may be neglected. He supposed that when a portion of base is presented at once to two acids, it is divided equally between them, or in the proportion of the quantities of the two acids, and that one acid can come to possess the base exclusively, only when it forms a volatile or an insoluble compound with that body, and thereby withdraws it from the solution, and from the influence of the other acid. His doctrine will be most easily explained by applying it to a particular case, and expressing it in the language of the atomic theory. The reaction between sulphuric acid and nitrate of potash is supposed to be as follows. On mixing eight atoms of the acid with the same number of atoms of the salt, the latter immediately undergoes partial decomposition, its base being equally shared between the two acids which are present in equal quantities; and a state of statical equilibrium is attained in which the bodies in contact are—

- (a) Four atoms sulphate of potash.  
Four atoms nitrate of potash.  
Four atoms sulphuric acid.  
Four atoms nitric acid.

The nitrate of potash, it is supposed, is decomposed to the extent stated, and no farther, however long the contact is protracted. But let the whole of the free nitric acid now be distilled off by the application of heat to the mixture, and a second partition of the potash of the remaining nitrate of potash is the consequence; the free sulphuric acid decomposing the salt till the proportion of the two acids uncombined in the mixture is again equal, when a state of equilibrium is attained. The mixture then consists of—

- (b) Six atoms sulphate of potash.  
Two atoms nitrate of potash.  
Two atoms sulphuric acid.  
Two atoms nitric acid.



On removing the free nitric acid as before, a third partition of the potash of the remaining nitrate of potash between the two acids on the same principle takes place, of which the result is—

(c) Seven atoms sulphate of potash.

One atom nitrate of potash.

One atom sulphuric acid.

One atom nitric acid.

The proportion of the two acids free being always the same. The repeated application of heat, by removing the free nitric acid, will cause the sulphuric to be again in excess, which will necessitate a new partition of the potash of the remaining nitrate of potash, till at last the entire separation of the nitric acid will be effected, and the fixed product of the decomposition be—

(d) Eight atoms sulphate of potash.

Here the affinity of the sulphuric and nitric acids for potash is supposed to be equal; and the complete decomposition of the nitrate of potash by the former acid, which takes place, is ascribed to the volatility of the latter acid, which, by occasioning its removal in proportion as it is liberated, causes the fixed sulphuric acid to be ever in excess.

Complete decompositions in which the precipitation of an insoluble substance occurs, were explained by Berthollet in the same manner. On adding a portion of baryta to sulphate of soda, the baryta decomposes the salt, and acquires sulphuric acid, till that acid is divided between the two bases in the proportion in which they are present, and at this point decomposition would cease, were it not that the whole sulphate of baryta formed is removed by precipitation. But a new formation of that salt is the necessary consequence of that equable partition of the acid between the two bases in contact with it, which is the condition of equilibrium; and the new product precipitating, more and more of it is formed, till the sulphate of soda is entirely decomposed, and its sulphuric acid removed by an equivalent of baryta.

According to these views of Berthollet, no decomposition should be complete unless the product be volatile or insoluble, as in the cases instanced. But such a conclusion is not consistent with observation, as it can be shewn that a body may be separated completely from a compound, and supplanted by another body, although none of the products is removed by the operation of either of the causes

specified, but all continue in solution and in contact with each other. Thus the salt borax, which is a biborate of soda, is entirely decomposed by the addition to its solution of a quantity of sulphuric acid not more than equivalent to its soda, although the liberated boracic acid remains in solution; for the liquid imparts to blue litmus paper a purple or wine-red tint, which indicates free boracic acid, and not that characteristic red tint, resembling the red of the skin of the onion, which would inevitably be produced by the most minute quantity of the stronger acid, if free. But if the borax were only decomposed in part in these circumstances, and its soda equally divided between the two acids, then free sulphuric, as well as boracic acid, should be found in the solution. The complete decomposition of the salt can be accounted for in no way but by ascribing it to the higher affinity of sulphuric acid for soda, than that of boracic acid for the same base.

According to the same views, on mixing together two neutral salts containing different acids and bases, and which do not precipitate each other, each acid should combine with both bases, so as to occasion the formation of four salts. Again, four salts, of which the acids and bases are all dissimilar, should react upon each other in such a way as to produce sixteen salts, each acid acquiring a portion of the four bases; and certain acids and bases, dissolved together in certain proportions, could have but one arrangement in which they would remain in equilibrio. Hence the salts in a mineral water would be ascertained by determining the acids and bases present, and supposing all the bases proportionally divided among the acids. But this conclusion is inconsistent with a fact observed in the preparation of factitious mineral waters, namely, that their taste depends not only on the nature of the salts, but also upon the order in which they are added. (Dr. Struve, of Dresden.) Before we can determine how the acids and bases are arranged in a mineral water, or what salts it contains, it may therefore be necessary to know the history of its formation. Instead of supposing the bases equally distributed among the acids in mixed saline solutions, it is now more generally assumed that the strongest base may be exclusively in possession of the strongest acid, and the weaker bases be united with the weaker acids; a mode of viewing their composition which agrees best with the medical qualities of mineral waters. It thus appears that the doctrines of Berthollet, by which the resulting actions between bodies in contact are made to depend upon their relative quantities or masses, and the physical properties of the products of their combination, to

the entire exclusion of the agency of proper affinities between the bodies, cannot be admitted as a true representation of the actual phenomena of combination.

#### CATALYSIS, OR DECOMPOSITION BY CONTACT.

An interesting class of decompositions has of late attracted considerable attention, which, as they cannot be accounted for on the ordinary laws of chemical affinity, have been referred by Berzelius to a new power, or rather new form of the force of chemical affinity, which he has distinguished as the *Catalytic force*, and the effect of its action as *Catalysis* (from *κατα*, downwards, and *λυω*, I unloosen). A body in which this power resides, resolves others into new compounds, merely by contact with them, or by an action of presence, as it has been termed, without gaining or losing anything itself. Thus an acid converts a solution of starch (at a certain temperature), first into gum and then into sugar of grapes, although no combination takes place between the elements of the acid and those of the starch, the acid being found free, and undiminished in quantity, after effecting the change. The same mutations are produced in a more remarkable manner by the presence of a minute quantity of a vegetable principle, *diastase*, allied in its general properties to gluten, which appears in the germination of barley and other seeds, and converts their starch into sugar and gum, which, being soluble, form the sap that rises into the germ, and nourishes the plant. This example of the action of a catalytic power in an organic secretion is probably not the only one in the animal and vegetable kingdoms, for it is not unlikely that it is by the action of such a force that very different substances are obtained from the same crude material by different organs. In animals, this crude material, which is the blood, flows in the uninterrupted vessels, and gives rise to all the different secretions; such as milk, bile, urine, &c. without the presence of any foreign body which could form new combinations. A beautiful instance of an action of catalysis was traced by Liebig and Wöhler in the chemical changes which the bitter almond exhibits. The application of heat and water to the almond, by giving solubility to its emulsin or albuminous principle, enables it to act upon an associated principle, amygdalin, of a neutral character, which then furnishes bodies so unlike itself as the volatile oil of almonds, hydro-

cyanic and formic acids. The action of yeast in fermentation is a more familiar illustration of a similar power. The presence of that substance, although insoluble, is sufficient to cause the resolution of sugar into carbonic acid gas and alcohol, a decomposition which can be effected by no other known means. Changes of this kind, although most frequent in organic compounds, are not confined to them. The binoxide of hydrogen is a body of which the elements are held together by a very slight affinity. It is not decomposed by acids, but alkalis give its elements a tendency to separate, slow effervescence occurring with the disengagement of oxygen, and water being formed. Nor do soluble substances alone produce this effect; other organic and inorganic bodies, also—such as manganese, silver, platinum, gold, fibrin, &c. which are perfectly insoluble—exert a similar power. The decomposition, in these instances, takes place by the mere presence of the foreign body, and without the smallest quantity of it entering into the new compound; for the most minute researches have failed in discovering the slightest alteration in the foreign body itself. The liquid persulphide of hydrogen, and a solution of the nitrosulphate of ammonia of Pelouze, are decomposed in the same way, and by contact of nearly all the substances which act upon peroxide of hydrogen. One remarkable difference, indeed, is observable, namely, that alkalis impart stability to nitrosulphate of ammonia, while acids decompose it, or the reverse of what happens with both the binoxide and bisulphide of hydrogen.\*

The phenomena referred to catalysis are of a recondite nature, and much in need of elucidation. The influence of platinum, formerly noticed, in disposing hydrogen and oxygen to unite, is probably connected with the catalytic power of the same metal, but is at present equally inexplicable. It would be unphilosophical to rest satisfied by referring such phenomena to a force of the existence of which we have no evidence. The doctrine of catalysis must be viewed in no other light than as a convenient fiction, by which we are enabled to class together a number of decompositions not provided for in the theory of chemical affinity, as at present understood, but which, it is to be expected, will receive their explanation from new investigations. It is a provisional hypothesis, like the doctrine of isomerism, for which the occasion will cease as the science advances.

\* Phil. Mag. 3d Series, vol. x. p. 489.



Feb. 2, 1849  
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## SECTION II.—CHEMICAL POLARITY.

*Illustrations from magnetical polarity.*—The ideas of induction and polarity, which now play so important a part in physical theories, were originally suggested by the phenomena of magnetism, which still afford the best experimental illustrations of them. A bar magnet exhibits attractive power which is not possessed in an equal degree by every particle composing the bar, but is chiefly localized in two points at or near its extremities. The powers, too, residing at these points are not one and the same, or similar, but different, indeed contrary, in their nature; and are distinguished by the different names of Austral magnetism and Boreal magnetism. The opposition in the mode of action of these powers is so perfect, that they completely negative or neutralize each other when residing in the same particle of matter in equal quantity or degree, as they are supposed really to exist in iron before it is magnetized; and they only signalize their presence when displaced and separated to a distance from each other, as they are in a magnet. A body possessing any such powers residing in it, which are not general but local, and not the same but opposite, is said (in the most general sense) to possess *polarity*.

In the theory of magnetism, it is found necessary to consider a magnet as composed of minute indivisible particles or filaments of iron, each of which has individually the properties of a separate magnet. The displacement or separation of the two attractive powers takes place only within these small particles, which are called the magnetic elements, and must be supposed so minute that they may be the ultimate particles or atoms themselves of the iron.

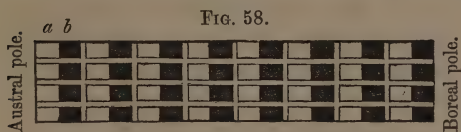


FIG. 58.

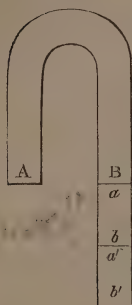
A magnetic bar may, therefore, be represented as composed of minute portions, *a b* in fig. 58 representing one such

Polar condition

portion; the right hand extremities of each of which possess one species of magnetism, and the left hand extremities the other. The unshaded ends being supposed to possess austral, and the shaded ends boreal magnetism, then the ends of the bar itself, of which these sides of the elementary magnets form the faces, possess respectively austral and boreal magnetism, and are the austral and boreal poles of the magnet. Such, then, is the polar condition of a bar of iron possessing magnetism, of which the attractive and repulsive powers

residing at the extremities are the results. Of the existence of such a structure the breaking of a magnet into two or more parts affords a proof, for it forms as many complete magnets as there are parts, new poles appearing at all the fractured extremities. A magnetic element, it is to be remembered, is itself insecable, like a chemical atom, so that the division must take place between magnetic elements.

FIG. 59.



When to the boreal pole B of a magnet (fig. 59), which may be of the horse-shoe form, a piece of soft iron,  $a\ b$ , wholly destitute of magnetic powers, is presented, a similar displacement of the magnetic forces of its elements occurs as in the magnet itself; or  $a\ b$  becomes a magnet by induction, and may attract and induce magnetism in a second bar  $a'\ b'$ ; both of which continue magnetic so long as the first remains in the same position, and under the influence of A B. These induced magnets must have the same polar molecular structure as the original magnet, but their magnetism is only temporary, and is immediately lost

when they are removed from the permanent magnet. The displacement of the magnetisms in these induced magnets commences at the extremity  $a$  of  $a\ b$ , in contact with B, which extremity has the opposite magnetism of B, (the different kinds of magnetism being mutually attractive,) and is the austral pole of  $a\ b$ ; and  $b$  is its boreal pole. Of  $a'\ b'$ , again, the upper extremity  $a'$ , in contact with  $b$ , is the austral, and the lower extremity  $b'$  the boreal pole, or  $b$  and  $b'$  have the same kind of magnetic power as the pole B of the original magnet, from which they are dependent. A third bar of soft iron placed at  $b'$  is likewise polarized, and the series of induced magnets

FIG. 60.

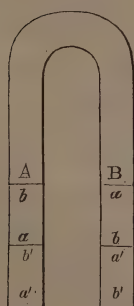
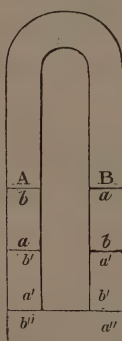


FIG. 61.



may be still farther extended, but the attractive powers developed in the different members of the series become less and less with their distance from the pole B of the original magnet.

A similar set of bars may be connected with A (fig. 60), which become temporary magnets also according to the same law, the lower extremities of this set being austral. On now uniting the lower extremities of both sets by another bar of soft iron  $a''\ b''$ , (fig. 61), either set renders  $a''\ b''$  a magnet, having its austral pole at

$a''$  and its boreal pole at  $b''$ ; and acting together, they communicate a degree of magnetism to the uniting bar greater than either set possessed before they were united. By this connexion, also, the inductive actions of each set of bars are brought to bear upon the other, and the attractive forces at all their poles are thereby greatly increased. In the most favourable conditions as to the size and connexion of the temporary magnets with relation to the primary magnet, each of the former, however numerous, acquires powers equal to those of the original magnet. This general enhancement of power in the induced magnets has been acquired, therefore, by completing the circle of them between A and B.

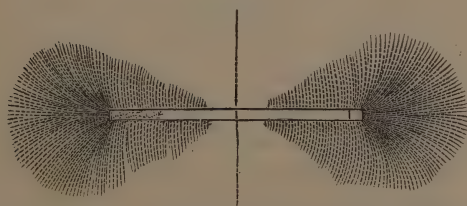
It is also important to observe, with a view to the future application of the remark, that a single bar of soft iron, or *lifter*, as  $b\ a$ , (fig. 62), connecting the poles of a magnet A B, not only acquires at  $b$  and  $a$  equal though opposite powers to the contiguous poles of

FIG. 62.



the magnet, but also reacts by induction on these poles themselves in a gradual manner, and increases their magnetism. The original magnetic forces of A and B are therefore increased, by the opportunity to act inductively, which the connecting bar affords them. The threads of steel filings which are taken up by a magnet, (see figure 63) illustrate the inductive action of magnetism, for each grain of steel is a complete magnet, and the threads a series of connected magnets. It will be

FIG. 63.



observed also that these threads diverge from each other; because, while unlike poles are in contact in each thread, which attract, like poles are in contact of adjoining threads

which repel. This repulsion of polar chains by each other, there will be occasion again to refer to.

*Atomic representation of a double decomposition.*—Chemical polarity, although less adapted for exhibition, is still more simple than magnetic polarity in its nature, while it is of a more fundamental character, and appears to be the basis of all other polarities whatever. In a binary compound,—such as chloride of potassium,—there reside two attractive powers, opposite in their nature; namely, the halogenous

affinity of the salt-radical chlorine, and the basylous affinity of the metal potassium. The atomic theory gives form to the molecule of chloride of potassium: one atom, Cl, being the seat of the halogenous, chlorous, or negative affinity (as we shall also call it); and the other atom, K, the seat of the basylous or positive affinity. A binary saline molecule is thus entirely similar to a magnetic element. We have to deal with two affinities only, —the chlorous and basylous. Atoms possessing different affinities attract each other; while atoms possessing the same affinity repel each other.

The two binary compounds, hydrochloric acid (chloride of hydrogen) and oxide of lead, when brought into contact, mutually decompose each other, forming chloride of lead and water:  $\text{H Cl}$  and  $\text{Pb O} = \text{Pb Cl}$  and  $\text{H O}$ . At the instant of acting upon each other, the two compound molecules must have a certain relative position. Under

(1), the basylous hydrogen of the hydrochloric acid is presented to the basylous lead of the oxide of lead, atoms which repel each other.

In (2) and (3), on the contrary, a basylous atom of one molecule is presented to a halogenous atom in the other, H to O in (2), and Cl to Pb in (3). These are attractive pairs; but, before they can enter

into new combinations, they must be released from the atoms with which they are already combined; which can be effected in (4), the only disposition of the polar molecules in which both attractive poles are together, and the actual decompositions and combinations possible: Cl is in contact with Pb at the same time that H is in contact with O, allowing the simultaneous formation of Pb Cl and H O. This is no more than the expression of a double decomposition in the language of the atomic theory.

It is further to be observed, that, in the original polar molecules (4), although approximation and combination are promoted by the attraction of the contiguous unlike poles, they are opposed by the mutual repulsion of the like poles; Cl repelling O, and Pb repelling H. This unfavourable influence of the repulsions is reduced to a minimum in the arrangement of several pairs of the hydrochloric acid

(1)



(2)



(3)



(4)

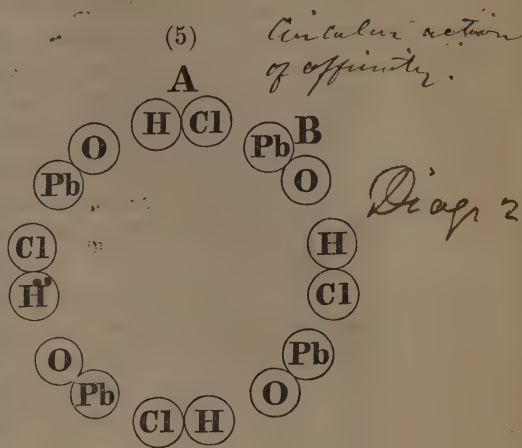


*Substitute  
Zinc for  
Lead in  
expt., also  
in diagrams  
& n. Then  
can pass  
easily  
into the use  
of "chlorous"  
& "zincous".*

*on Pbous*  
Chemical Affinities  
of Salt rad.  
Halogenous  
Chlorous  
Negative  
of Basylous  
Zincous  
Positive



and oxide of lead molecules to form one circle. In (5), four pairs of the polar molecules are symmetrically placed; HCl alternately with PbO, and the attractive poles of the different molecules together. Affinities tending to a simultaneous formation of chloride of lead and water are equally favoured in this arrangement, as in (4); while the mutual repulsion of the like atoms,—such as the H and Pb, or the Cl and O of the adjoining molecules A and B—is less, as these like atoms are more distant from each other in the circular arrangement. It is obvious that



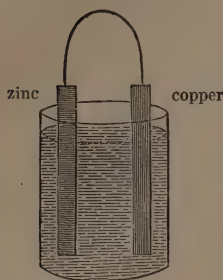
the repelling atoms will be more distant the larger the circle, or the more nearly a segment of it approaches to a straight line. This arrangement of many pairs in a circle, being a condition of equilibrium, is a necessary one, and must take place in all double decompositions occurring in a liquid where the binary molecules are free to move. The formation of such polar circuits explains the ready occurrence of double decompositions; but it is of still more importance, as being the simplest and most intelligible exhibition of a voltaic circle.

Included in Lead  
by J. Bannister  
Feb. 5, 1849  
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*a saline substance*  
*Action of an acid upon two metals in contact.*—When a plate of zinc is plunged into hydrochloric acid, a chemical change of a simple nature ensues; the metal dissolves, combining with the chlorine of the acid and displacing its hydrogen, the gas-bubbles of which form upon the zinc plate, increase in size, detach themselves, and rise through the liquor to its surface. The solution of zinc, when effected by its substitution for hydrogen, as in this experiment, is attended by a train of extraordinary phenomena, which become apparent when a second metal, such as copper, silver, or platinum, is placed in the same acid fluid, and allowed to touch the zinc, the second metal being one upon which the fluid exerts no solvent action, or a less action than upon zinc.

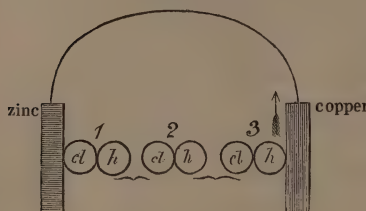
The zinc plate being connected by a metallic wire with a copper plate, as represented in fig. 64, and both dipped together in the hydrochloric acid, the zinc only is acted upon, and dissolves as rapidly as before; but much of the hydrogen gas now appears upon, and is

FIG. 64.



acid extending from the zinc to the copper, and may be conceived by the diagram on the margin, in which each pair of associated

FIG. 65.

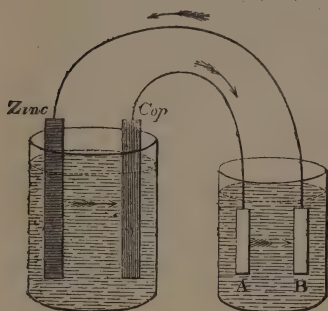


circles marked *cl* and *h* represents a particle of hydrochloric acid, The chlorine *cl* of particle 1 in contact with the zinc combining with that metal, its hydrogen *h* combines, the moment it is set free, with the chlorine of particle 2, as indicated by the connecting ~~bracket~~ *brace* below, and liberates the hydrogen of that particle, which hydrogen forthwith combines with the chlorine of particle 3, and so on through a series of particles of any extent till the decomposition reaches the copper plate, when the last liberated atom of hydrogen (that of particle 3, in the diagram) not having hydrochloric acid to act upon, is evolved and rises as gas in contact with the copper plate.

It is to be observed that this succession of decompositions and recombinations leading to the discharge of the hydrogen at the copper, does not occur at all unless that plate be in metallic connexion with the zinc, by means of a wire, as in the figure, or by the plates themselves touching without or within the acid fluid. This would seem to indicate that while the decomposition travels from the zinc to the copper through the acid, some force or influence is propagated at the same time through the wire, from the copper back again to the zinc. That something does pass through the wire in these circumstances is proved by its being heated, and by its temporary assumption of certain electrical and magnetic properties. Whether anything material does pass, or it is merely a vibration or vibratory impulse, or a certain induced condition that it is propa-

gated through the molecules of the wire, of which the electrical appearances are the effects, cannot be determined with certainty. But a power to effect decomposition, the same in kind as that occurring in the acid jar, and which acts in the same sense or direction, is propagated through the wire, and appears to be fundamental to all the other phenomena.

FIG. 66.



Let the wire, supposed to be of platinum, connecting the zinc and copper plates, be divided in the middle, and the extremities A and B of the portions attached to the copper and zinc plates respectively be flattened into small plates, and then dipped at a little distance from each other in a second vessel containing hydriodic acid. Iodine will soon appear at A, although that element is incapable of combining with

the substance of the platinum, and hydrogen gas will appear at B. If the connecting wire and the small plates A and B were of zinc or of copper, the hydriodic acid would be decomposed precisely in the same manner, but the iodine as it reached A would unite with the metal and form an iodide. Supposing a decomposing force to have originated in the zinc plate, and to have circulated through the hydrochloric acid in the jar to the copper plate, and onwards through the wires and the hydriodic acid back to the zinc, as indicated by the direction of the arrows, then the hydrogen of the hydriodic acid has followed the same course, and been discharged against the metallic surface to which the arrow points.

The solution of the zinc in hydrochloric acid which develops these powers, acting at a distance, is not itself impeded, but on the contrary is promoted by exerting such an influence: for, placed alone in the acid, that metal scarcely dissolves at all, if pure and uncontaminated with other metals, or if its surface has been silvered with mercury; but it dissolves with rapidity when a copper plate is associated with it in the same jar, in the manner described. Hence the decomposing power which appears between A and B cannot be viewed as actually a portion of that which causes the solution of the zinc in the hydrochloric acid, for that force has suffered no diminution in its own proper sphere of action.

This combination of metals and fluids is known as the *simple voltaic circle*.

To explain the phenomena of the voltaic circle, the existence of a substantial principle, the electric fluid, has been assumed, of such a nature that it is readily communicable to matter, and capable of circulating through the voltaic arrangement, carrying with it peculiar attractive and repulsive forces which occasion the decompositions observed. A vehicle was thus created for the chemical affinity which is found to circulate. But it is generally allowed that this form of the electrical hypothesis has not received support from observations of a recent date, particularly from the great discoveries of Mr. Faraday, which have completely altered the aspect of this department of science, and suggest a very different interpretation of the phenomena. All electrical phenomena whatever are found to involve the presence of matter, or there is no evidence of the independent existence of electricity apart from matter; so that these phenomena may really be exhibitions of the inherent properties of matter. The idea of anything like a circulation of electricity through the voltaic circle appears to be abandoned. Electrical induction, by which certain forces are propagated to a distance, is found to be always an action of contiguous particles upon each other, in which it is unnecessary to suppose that any thing passes from particle to particle, or is taken from one particle and added to another. The change which a particle undergoes takes place within itself, and it is looked upon as a temporary development of different powers in different points of the same particle. The doctrine of polarity has thus come to be introduced into the discussion of electrical phenomena.\*

One reason for retaining the theory of an electric fluid or fluids is, that it affords the means of expressing in distinct terms those strictly physical laws which are reputed electrical; and for many purposes such an hypothesis is unquestionably useful, if not absolutely necessary; but it has nothing to recommend it in the description of the chemical phenomena of the voltaic circle. These admit of a perfectly intelligible statement, when viewed as an exhibition of

\* For Mr. Faraday's views, the eleventh and subsequent series of his Researches, in the Philosophical Transactions for 1836, and the following years, may be referred to. He has favoured the scientific world with a reprint of the whole series: Faraday's Experimental Researches in Electricity: R. and J. E. Taylor, London, 1839. The subject is also systematically treated in the work of the late Professor Daniell, entitled an Introduction to the Study of Chemical Philosophy, which may be consulted with advantage.

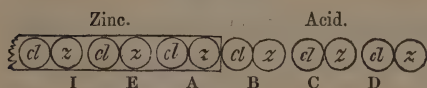


ordinary chemical affinity, acting in particular circumstances, without any electrical hypothesis.

*Polarity of the arrangement.*—It is to be assumed that the zinc and hydrochloric acid are both composed of particles, or molecules, which are susceptible of a polar condition. Of hydrochloric acid, the chemical atom is the polar molecule, and it therefore consists of an atom of chlorine and an atom of hydrogen associated together. The polar molecule of zinc may be supposed, for a reason which will afterwards appear, to consist of a pair likewise of associated atoms, which, however, are in this body both of the same element. The powers appearing in a polar molecule of zinc and of hydrochloric acid are the same. One pole of each molecule has the basylous attraction, or affinity, which is characteristic of zinc, or *zincous* attraction, and may be called the zincous pole; while the other has the halogenous attraction, or affinity, which is characteristic of chlorine, or *chlorous* attraction, and may be called the chlorous pole.

Zinc and acid in contact may therefore be represented (fig. 67)

FIG. 67.



by trains of associated pairs of atoms. In the molecule of hydrochloric acid B, which is next the zinc, the chlorine atom forms the

chlorous pole, and is turned towards the zinc, the fluidity of the acid allowing its molecule to take that position, which may be indicated by inscribing *cl* in the circle which represents the chlorine atom. The other atom of the molecule B, or the hydrogen, is the opposite, or zincous pole, and is marked *z*. Of the two atoms forming the polar molecule A of the zinc, the exterior atom which is in contact with the acid has thereby zincous attraction developed in it, and becomes the zincous pole, while the interior becomes the chlorous pole, as indicated in both by the inscribed letters. This polar condition of the zinc must be supposed the necessary and immediate consequence of its contact with the polar acid.

But each of these particles throws a train of particles of its own kind into a similar state of polarity: A, the contiguous particles E and I of the zinc, and B the contiguous particles C and D of the acid. For *cl* of A becoming a chlorous pole, develops near it in an opposite, or zincous pole in *z* of E, and a chlorous pole in *cl*, the more remote extremity of E; in the same manner as the austral pole of a magnet develops, by induction, a boreal and austral pole in a piece of soft iron

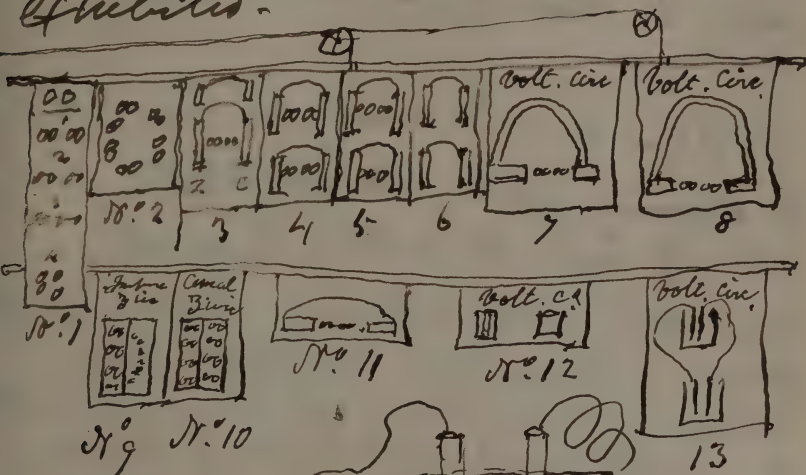
applied to it. And as the induced magnet, thus formed, will react upon a second piece of iron, and render it also magnetic, so the polarized particle E renders I similarly polar. The polar arrangement of the particles C and D of the acid is produced by B in the same manner. But as in a series of induced magnets (fig. 59, page 236), the magnetism acquired diminishes with the distance from the pole of the original magnet, so in trains of chemically polarized molecules, such as A, E, I and B, C, D, the amount of polarity developed in each molecule will diminish with the distance from the sources of induction A and B; I being polarised to a less degree than E, and D than C.

In the electrical theory of the voltaic circle as modified by Mr. Faraday, the zinc and hydrochloric acid are equally supposed to have a polarizable molecule. The polarity is also developed in these molecules by their approximation or contact. The molecule of hydrochloric acid is supposed to contain the positive and negative electricities, which possess contrary powers, like the two magnetisms, and are in combination and neutralize each other, in the non-polar condition of the molecule. But the contact of zinc causes the separation of the two electricities in the acid molecule, its atom of chlorine next the zinc becoming negative, and its atom of hydrogen positive. The electricities of the zinc molecule are separated at the same time, the side of the molecule next the acid becoming positive, and the distant side negative. The positive and negative sides of the two different molecules are thus in contact, the different electricities, like the different magnetisms, attracting each other. Hence, one side of each molecule is said to be positive instead of zincous, and the other side to be negative instead of chlorous. Polarity of the molecule is supposed in both views, but on one view the polar forces are the two electricities, on the other two chemical affinities. The difference between the two views is little more than nominal, for in both the same powers and properties are ascribed to the acting forces. The electricities are supposed to be the cause of the chemical affinities, but it may with equal justice be assumed that chemical affinities are the cause of the phenomena reputed electrical. One set of forces only is necessary for the explanation of the phenomena of combination, and the question is, whether are these forces electrical or chemical? Shall electricity supersede chemical affinity, or chemical affinity supersede electricity? If the electricities should be retained, in discussing the voltaic circle, their names might well be changed, the positive called zincous electricity,

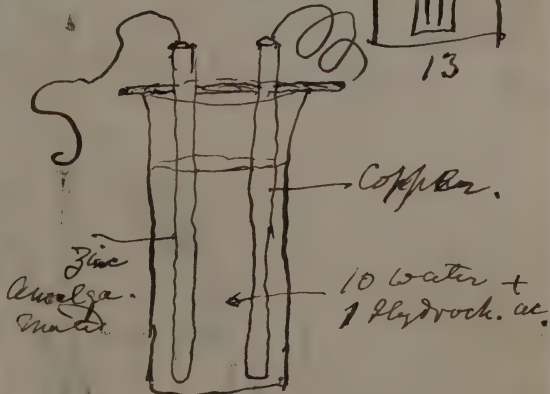
June 27, 1852.

# Chemical Polarity.

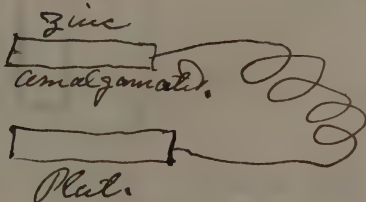
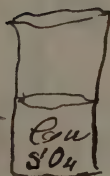
First Lecture.  
The following are diagrams  
exhibited:



Expt. 1.

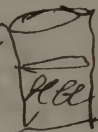


Expt. 2.

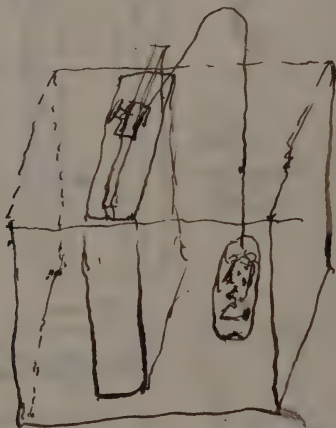


Acid dilute so-  
lution of 2 lph. or  
chloride of cop.

Experiment 2. is to show deposition of Copper on the platinum plate & first dip same pair into dilute hydrochloric acid in similar jar - to show hydrogen on platinum.



Expt. 3. It would be useful to operate with the electrolytic cell - to begin the expt.; but this was not overtake. Square glass trough. Zinc plate coupled to the matrix. Porous cell. Sulphuric acid to 10. Acid solut. Sulphate of Copper.



The shut zinc does not require



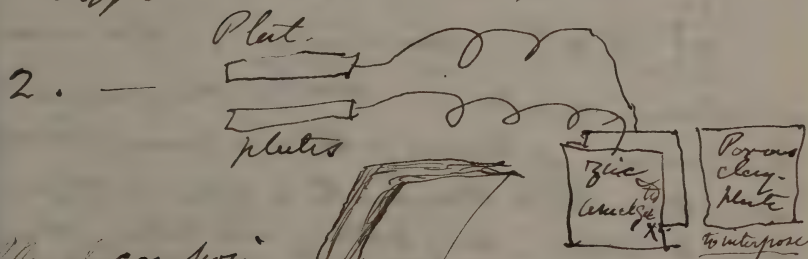
to be amalgamated, I should not be so large as the object - to prevent a rapid & powdery precipitation of copper.

Illustrated by Diagrams 11 and 7.

## Second Lecture.

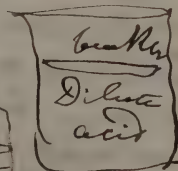
Same diagrams.

Expt. 1. The electrolytic cell.



The decomposition of iodide of potassium.

Paper, with solution of Iodide of Potassium



They have starched iodide solution but

Page 4

but not essential.

Above illustrated by Diagram 8  
Expt. 9. Pure zinc in  
foot glass - dilute acid  
Rend. improved by <sup>drops of</sup> dilute  
arsenious acid.

Diagram 9.

Expt. 4.  
Amalgam -  
motion of plate  
of zinc

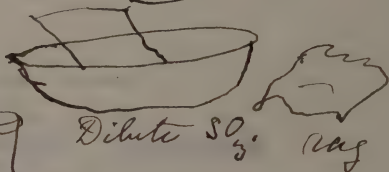
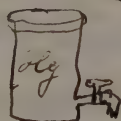


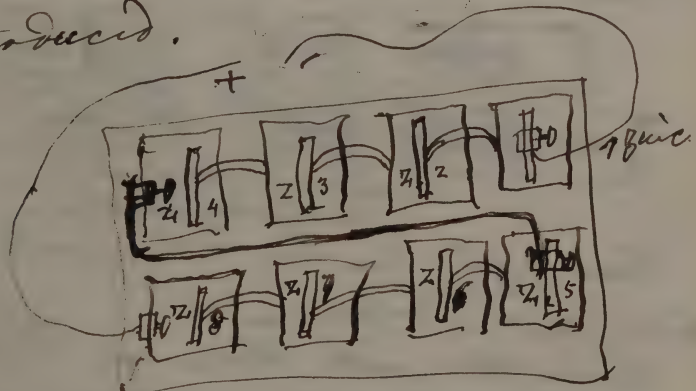
Diagram 10.

3<sup>rd</sup> & 4<sup>th</sup> Lectures. Some  
of above expts. with diagrams &  
Exhibition of Brown of cups (4 glasses), Gravel.  
Shanks. Used Maynooth 4 cells - but per-  
haps 8 better. only battery used today. In  
plate glass cells - Iodide pot. & starch (last),  
KCl with indigo;  $SO_2$  <sup>NaO</sup> with blue litmus but  
cabbage later, or a second expt. with turmeric.  
First expt. the plates in water, & then add  
 $SO_2$ . The Voltmeter with plate glass  
trough, own single tube for gases. Pair  
of tubes from Met. Phil: stop when nearly full  
of gas.

# Chemical Polarity continued

## Fifth Lecture.

Daniell's battery - Diagram of  
one cell: on rail before board.  
grooves. The whole series in  
a row to left hand.  
Butler's carbon-zinc in iron, left hand  
Manganese charged. Equal  
vols. of oil of vitriol & nitric  
acid 1.35 or stronger in iron  
cell. Sulphuric acid 1 vol to 8  
vol water in porous cells, which  
should be dry before the  $SO_3$  is  
introduced.

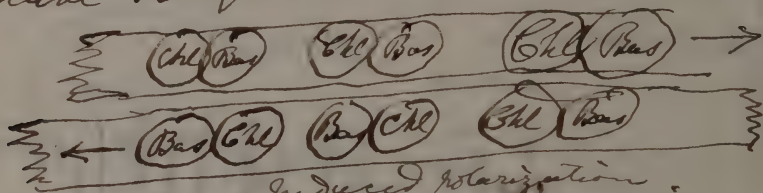


last view

The last battery was placed on  
lecture table to ~~left~~ right hand.  
Borrowed from Mat. Phil. Prat  
examine & replace injured plates.

Used also own Daniell's in jar  
jar with water slightly acidu-  
lated. Coil for shocks borrowed  
from Hospital: clamp it to  
table.

In Magnetic apt., begin first  
with induced current polarization,  
Thom diagram to illustrate



Induced polarization.  
Last <sup>ing</sup> paler colours.

Iron cylinder in helix, with nails,  
first apt.; before -  
Horse shoe, with stone, on tripod,  
right side, to follow. Door mat  
from Prof's room.



above previously described ~~holding~~ rectangle,  
+ the ~~half~~ <sup>half</sup> ~~monometer~~.

In heating appts., the ~~Keen~~ <sup>Keen</sup> ~~smooth~~  
cells acted only on the ~~thinest~~  
harpsichord & platinum wire.  
Procure the compound silver  
& plat. wire.

To do justice to these appts.  
one large Grove should be used.

The small Grove acts feebly:  
the cells appear to be no longer  
sufficiently porous.

In the Electrotypic cell, a  
plate from Grove's large battery  
was used.

Had on Board (first day)  
Chemical Apparatus.

Chlorophorus  
Halogenous  
Negative  
            
(in red)

Barytes  
Positive  
+  
(in ~~the~~ white)

Afterwards, the series of  
"Most Positive" - Potassium V.  
in two columns -

By Thermo-electricity & bars  
of bismuth & antimony - with  
galvanometer. Diagram -

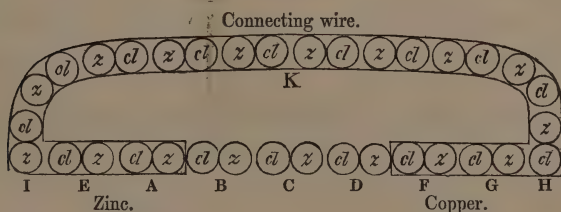
and the negative chlorous electricity, which express (as will appear more clearly afterwards), the nature of the chemical affinities with which these electricities are invested, and of which they are indeed constituted the sole depositories. The propagation of the effects to a distance is supposed to take place by the polarization of chains of molecules, on the electrical as well as chemical theory of the voltaic circle; so that the explanations which follow, although expressed in the language of the chemical theory, are the same in substance as those which are given on the electrical theory as now understood.

If the attractions of the respective zincous and chlorous poles of A and B which are in contact, rise to a certain point, the atom *z* of A is detached from the mass of metal, and combines with the atom *cl* of B, which last atom is disengaged at the same time from its hydrogen. Chloride of zinc is produced and dissolves in the liquid, while hydrogen is disengaged and rises from the surface of the metal; or we have the ordinary circumstances of the solution of an isolated mass of zinc in hydrochloric acid.

## SIMPLE VOLTAIC CIRCLE.

*Circle with the connecting wire unbroken.*—When the zinc is pure, or its surface amalgamated with mercury, the zincous and chlorous attractions of the touching poles of A and B are not sufficiently intense to produce these effects, and combination does not occur. Let a copper plate F G H (fig 68), be then introduced

FIG. 68.



into the acid, and connected by a metallic wire H K I with the zinc. The particles of the acid assume chlorous and zincous poles as before; so also do those of the zinc, and the chain of polar molecules is now continued through the zinc and wire to the copper, the exterior particle F of which, it will be observed, comes thereby to present a chlorous pole to the acid. The contiguous particle D of acid is thus exposed to a second induction from the chlorous polarity

of the copper, which increases the zincous polarity of the side of D next F, and, therefore, cooperates in enhancing the polar conditions already assumed by the chain of acid particles extending between the two metals. An endless chain or circle of polar molecules symmetrically arranged is thus formed, such as exists in a magnet of which the poles are united by a lifter, in which every particle in the chain has its own polar condition elevated by induction, and at the same time does itself react upon and elevate the polar condition of every other particle in the chain. The result of this is that the primary attraction of the zinc atom  $z$  of A, for the chlorine,  $cl$  of the hydrochloric acid B, is increased, and attains that degree of intensity at which the resistance to the impending combination is overcome, and the  $z$  and  $cl$  of A and B unite. But in a circle of polar molecules, in which the condition of any one molecule determines and is determined by that of every other, the intensity of the polar condition is necessarily the same in every element of the circle. The chemical polarity, therefore, of the other particles forming the chain, must increase to an equal degree as with A and B, when the circle is completed, and the same change must now occur in all of them that has occurred in A and B. The pole of B next C is intensely zincous, while that of C next B is intensely chlorous, whence the chlorine and hydrogen  $cl$  and  $z$  of these two particles combine together. At the same time, and for the same reason, the hydrogen  $z$  of C unites with the chlorine  $cl$  of D; and so on, through a chain of particles of hydrochloric acid of any length, till the copper is reached, when the last acid particle, D in the figure, yields its hydrogen  $z$  to the chlorous pole of the copper  $cl$ . But *the hydrogen not being capable of combining permanently with the copper, is liberated as gas upon the surface of that metal.*

Some internal change of a similar character appears to take place in the chain of polarized molecules extending through the metals themselves—a series of molecular detachments and re-attachments, among the atoms of their polar molecules, like the decompositions and recompositions in the acid, causing evolution of heat and other phenomena, generally reputed electrical, which the zinc and copper plates and the connecting wire exhibit.

*Amalgamation of the zinc plate.*—The polar molecule of the metals has been assumed to contain two atoms (like that of the acid), with the view of assimilating these intestine changes in the solid to those occurring in the fluid portion of the voltaic circuit, and



also because it appears to account for the advantage of amalgamating the zinc surface. In the amalgamated plate, it is not zinc itself, but a chemical combination of mercury and zinc, which is presented to the acid, in which mercury is the negative element, and which might, therefore, be called a hydrargyride of zinc. That combination likewise is *fluid*. It must constitute the polar molecule, which will then consist of an atom of mercury as chlorous pole, and an atom of zinc as zincous pole, and not of two atoms of zinc. Such metallic molecules being capable of movement from their fluidity will place themselves, in forming a polar chain, with their unlike poles together, as the fluid acid particles arrange themselves. So that in an amalgam of zinc, of which A, E, and I, are polar molecules (fig. 68), all the atoms marked *cl* are mercury, and those marked *z* are zinc. It thus follows that, when by contact with an acid the amalgam is polarized, it presents a face of zinc only to the acid. If the mercury were exposed to the acid, that metal would completely derange the result, acting locally like a copper plate, as will afterwards be explained.

*This last  
the principal  
source of  
advantage  
in amalgamating.*

The previous combination of the zinc (with mercury) likewise prevents that metal from yielding easily to the chlorine of hydrochloric acid; and the zinc of the amalgam is, therefore, not dissolved, till the affinities are enhanced by the introduction of a copper plate into the acid, and the formation of a voltaic circle.

It would thus appear that zinc, associated with copper, dissolves more readily in the acid than when alone, because the attraction or affinity of the zinc for chlorine is increased by the completion of a circle of similarly polar molecules, in the same manner as the magnetic intensity at one of the poles of a magnet is increased on completing the circle of similarly polarized elements, by connecting that pole by means of soft iron with the other pole (Fig. 62, page 237).

Although the terms of the electrical hypothesis are at present avoided, still it will be convenient to denominate the zinc, being the metal which dissolves in the acid, the active or *positive* metal, and the copper, which does not dissolve, the inactive or *negative* metal of the voltaic circle.

Looking to the condition of the two connected metals in the acid, it will be observed that the surface of the zinc presented to the acid has zincous affinity, or is zinco-polar, but the surface of the copper presented to the acid has, on the contrary, chlorous affinity, or is chloro-polar. Such a condition of the copper is necessary to the propagation of the induction; and the advantage of copper or pla-

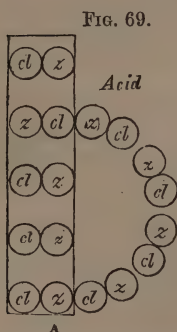
*Feb. 6  
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25-0

tinum as the negative metal in a voltaic arrangement depends upon there being little or no impediment to either of these metals assuming the chlorous condition, that can arise from the peculiar affinity of the metals named for the chlorine of the acid; an affinity which tends to cause them to be superficially zincous instead of chlorous. If the second metal were zinc, the surface of it would be disposed to dissolve in the acid, and becoming on that account zincous, would induce a polarization in the intermediate acid in an opposite sense from that induced by the first plate of zinc; which counter polarizing actions would mutually neutralize each other. The acid between the two zinc plates would be like a piece of iron connecting two like magnetic poles, which itself is not then polarized.

But if one of the two zinc plates were less disposed to dissolve in the acid than the other, from the physical condition of its surface, from the acid being weaker there, or from any other cause, then the plate so situated might become negative to the other, and a voltaic circle of weak power be established, in which both metals were zinc.

*Impurity of the zinc.*—If zinc is alone in the acid, and every superficial particle of the metal equally disposed dissolve, then the zinc everywhere exposes a surface in a state of zincous polarity; and a polar circle in the liquid, starting from one particle of the zinc and returning upon another, cannot be established, as this requires that a part of the zinc surface be chlorous. But if the zinc contains on



its surface a single particle of copper, a chlorous pole is created, upon which an inductive circle starting from an adjoining particle of zinc, A, (fig. 69), and passing through the liquid, may return as shewn in the figure. It is the forma-

tion of such circles that causes impure zinc, which is contaminated by other metals, to dissolve so much more quickly in an acid than the pure metal. Why such circles are not formed when the positive metal in combination with the zinc is mercury, which forms a fluid alloy, has already been accounted for; and the nature of the evil which might otherwise attend the amalgamation of the zinc is now evident.

The whole chain of polar molecules in the voltaic circle admits of a natural division into two segments, the acid or liquid segment B C D (fig. 68), and the metallic segment, A K F, each of which has a pair of poles, the unlike poles of the two segments being opposed to each other. The pole at B of the acid portion is chlorous,

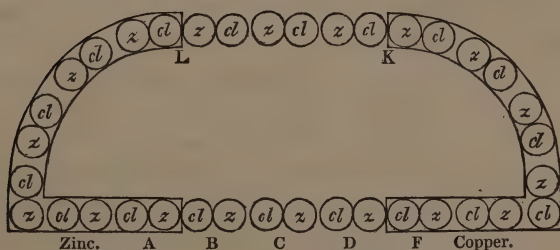
and is opposed to the zincous pole at A of the metallic segment; while the pole of the liquid segment at D is zincous, and is opposed to the chlorous pole of the metallic segment at F. The distribution of polarity in these two segments is, therefore, the same as in two magnets with their unlike or attracting poles in contact.

Such, then, is the action of affinity by induction, which the mere introduction of zinc and copper in contact into the same acid liquid is sufficient to develop, and which accounts for the discharge of the hydrogen upon the surface of the copper in such an arrangement, the remarkable phenomenon by a description of which this subject was introduced.

*Circle with the connecting wire broken.*—It remains for us to apply the same principles to explain the additional phenomena of the second case described, in which the connecting wire, supposed to be of platinum, between the zinc and copper plates, is divided, and the broken extremities introduced into hydriodic acid (fig. 68, page 245).

Broken at any point, as at K, (Fig. 68), it is evident that if the polarised condition be still sustained, the portion of the metallic segment connected with the copper plate will terminate with a zincous pole at K, and that connected with the zinc with a chlorous pole; which may be indicated respectively by K and L, in fig. 70.

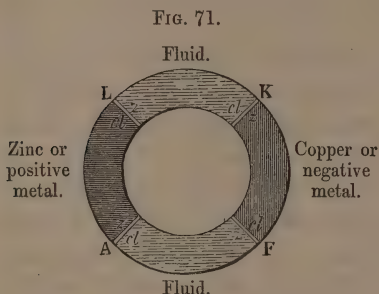
FIG. 70.



When hydriodic acid is interposed between K and L, the breach is repaired by the polarization of a chain of particles of that acid. The extremity K, being zincous, induces chlorous polarity in the side of the hydriodic acid particle which it touches; in consequence of which the iodine atom (the analogue of chlorine) of the hydriodic acid molecule is presented to that pole, and liberated there when decomposition occurs. The extremity L of the zinc or positive metal element is chlorous, and therefore induces zincous polarity in the particle of hydriodic acid which it touches, and hydrogen (the analogue of zinc) is liberated there. The polarity in an induced

circle must necessarily be of equal intensity at every point in it, and being sufficient at A to cause the decomposition of the hydrochloric acid, must also decompose the hydriodic acid between K and L; otherwise it is never established at A, nor anywhere else.

In the present arrangement, the voltaic circle is broken into four segments, or has four polar elements, every terminal pole of which is in contact with a pole of a different name; and the whole arrangement may be compared to a circle of four magnets with the attractive poles in contact.



These elements are:—First, the zinc plate or positive metal, A L, of which the end at A, in the hydrochloric acid (fig. 71), has zincous affinity, and the end faced with platinum at L, in the hydriodic acid, chlorous affinity.

Secondly, the body of hydrochloric acid, A F, between the zinc and copper plates, of which the surface at A, in contact with the positive metal, has chlorous, and that at F, in contact with the negative metal, zincous affinity.

Thirdly, the copper or negative metal F K, of which the end at F in the hydrochloric acid has chlorous affinity, and that faced with platinum at K in the hydriodic acid, zincous affinity.

And fourthly, the body of hydriodic acid, K L, between the zincous and chlorous poles of the negative and positive metals, of which the surface K, in contact with the negative metal, is chlorous, and the surface L, in contact with the positive metal, zincous.

In every voltaic circle employed to produce decomposition these four elements are to be looked for. Hereafter, in adverting to any one of these elements, it will be sufficient to confine our notice to its terminal polarities or affinities, without recurring to the polarized condition of the element itself, upon which its terminal affinities depend.

*Feb. 8, 1849*

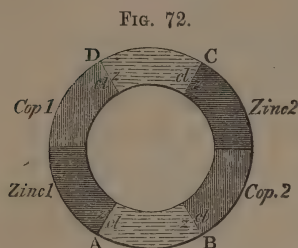
#### COMPOUND VOLTAIC CIRCLE.

In both the arrangements described there is only one source of polarizing force, namely, the action between the zinc and acid at A. But a circle of a similar nature may be constructed embracing within itself two or more of such primary sources of polarizing power, and

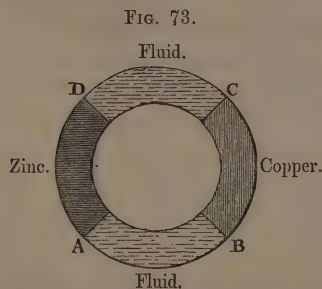


the intensity of the polar condition of the whole circle be thereby greatly increased.

Figure 72 represents such a circle, in which there are two zinc plates, both supposed to be in contact with hydrochloric acid, namely at A and at C, and a copper plate attached to each of these zincs. The polar condition of such a circle will easily be observed. By the contact of the acid and zinc at A, a zincous pole is established there in the first zinc plate, and a chlorous pole in the



acid, which are so inscribed in the diagram. These occasion the formation of a chlorous pole at D in the first copper, the united zinc and copper A D forming together one polar element; and a zincous pole at B in the acid, the column A B of acid being the second polar element. The further effect of the induction is to produce a chlorous pole at B in the second copper, of which the corresponding zincous pole is at C, in the second zinc; the united zinc and copper B C forming together a third polar element. And, as a last consequence of the inducing force originating at A, the column of acid between C and D becomes a fourth polar element of the circle, having a chlorous pole at C and a zincous pole at D. Now it will be observed that the chemical affinity between the acid and zinc at C tends to produce the same polar conditions at that point as are already established there from the effect of induction. The extremity of the zinc plate at C is in fact zincous, both primarily and by induction; and the acid in contact with it chlorous, likewise both primarily and by induction; and generally, throughout the whole circle, the polar conditions determined by the second chemical action at C are the same as those determined by the first action at A.

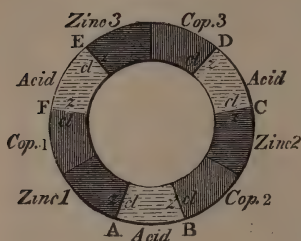


the last arrangement, the inductive actions are in the same direction, and favour each other; but a circle may be constructed in which the inductions, being in opposite directions, oppose and neutralize each other. Thus if A D (fig. 73) be entirely zinc, both its extremities being exposed to acid, will tend equally to be zincous.

In the same way, if B C be entirely copper, the condition of both its extremities will be chlorous, from the action of the acid on the two ends of the zinc; and, consequently, the elements of such a circle could have no polarity.

A circle is represented in fig. 74, containing three sources of polarizing force. It consists of three alternations of copper and zinc sym-

FIG. 74.



metrically arranged, and forming three polar elements F A, B C, and D E, with three acid columns between these alternations, which form three additional polar elements, A B, C D, and E F. The number of alternations of copper and zinc with acid may obviously be increased to any extent, and the chemical action of the acid on the zinc in each alternation is found to increase in

a marked manner up to the number of 10 or 12 alternations. This increase of the affinity is undoubtedly owing to the favouring inductive action which the chemical actions at the different points have upon each other. Such a compound circle may be compared to a number of magnets disposed in a circle with their attracting poles together, of which each would have its magnetic intensity exalted by induction from all the rest. When such a circle is broken at any point, all chemical action and polarization cease till contact is again made, and the circuit completed. The polarization, too, being the result of a circular induction involving so many lines or chains of particles, cannot, when once established, be more or less at any one point in the circuit than at others. The resulting chemical action must, therefore, be every where equal in the circle, and consequently the same quantity of zinc be dissolved, and hydrogen evolved in each acid.

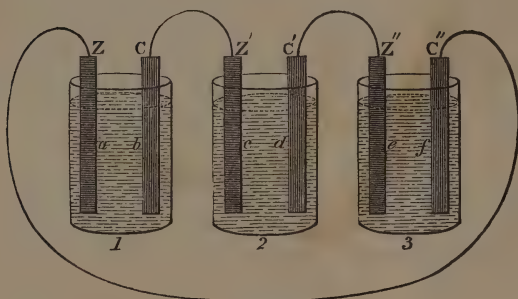
If any metallic element of this compound circle be broken, and a polarizable liquid be interposed between the metallic extremities so as to complete the circuit, decomposition occurs in that liquid as in the simple interrupted circle (fig. 70). But the polarizing influence of the compound circle being of high intensity, more numerous and difficult decompositions are effected by means of it than by the simple circle. The compound voltaic circle is indeed a decomposing instrument of great efficiency.

If, in this arrangement, the position of one of the metals in the series be reversed, so that a zinc is where a copper should be, then,

by the action of the acid on that zinc, polarization in the wrong direction is occasioned, which greatly diminishes the general polarity of the circle, reducing it in an arrangement of ten alternations to one-fourth, according to Mr. Daniell.

*Voltaic battery.*—In the first of the two annexed diagrams (fig. 75) is represented a compound circle, such as is employed to

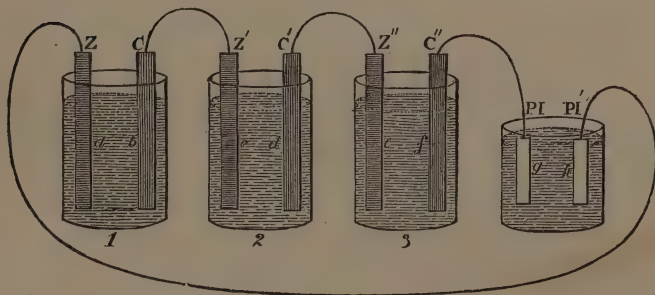
FIG. 75.



produce decomposition, and called a voltaic battery, consisting of three acid jars, each of which contains a zinc and copper plate, and which are termed active cells, as they are sources of polarizing power, from the action of acid upon zinc which takes place in them.

In the second diagram (fig. 76), the same arrangement is repeated,

FIG 76.



with the addition of a third jar, termed the decomposing cell, which contains any binary polar liquid, with two platinum plates immersed in it. Each copper, it will be seen, is connected by a wire with the following zinc; and, in the first diagram, the copper in the third cell

$C''$  is immediately connected with the zinc in the first cell  $Z$  by a wire, and the circuit thus completed. The polar elements in the circle of the first diagram, it will be found, are six in number; namely, the three acid columns between the metals in the cells  $a\ b$ ,  $c\ d$ , and  $e\ f$ ; and the three pairs of zinc and copper plates, each of which pairs forms a single polar element, of which the surface of the zinc is the zincous, and the surface of the copper the chlorous pole. In the second diagram, one of these metallic elements  $Z\ C''$  is divided, and a polar liquid  $g\ h$ , in the cell of decomposition, interposed between the broken extremities  $Pl$  and  $Pl'$ . To ascertain the polar condition of the extremities, or the terminal platinum plates in the decomposing cell, it is to be observed that  $Pl'$  with  $Z$  forms one polar element, of which  $Z$  being a zincous pole,  $Pl'$  must be a chlorous pole. Again,  $Pl$  with  $C''$  forms one polar element, of which  $C''$  being a chlorous pole,  $Pl$  must be a zincous pole. Now, the platinum plates  $Pl$  and  $Pl'$ , which are thus zincous and chlorous, are disposed in the decomposing cell, in regard to one another,—the first to the left, and the second to the right, as the zincous and chlorous plates (the zinc and copper) also are arranged in the active cells. It will be convenient to distinguish by names the poles which these terminal platinum plates constitute, as they are much more frequently referred to, and of greater consequence than any other poles in the voltaic battery, when used as an instrument of decomposition, as it constantly is. The chlorous plate  $Pl'$ , which is in connexion with a zinc plate  $Z$ , may be called the *chloroid* (like chlorine), and the zincous plate  $Pl$ , which is connected with a copper plate  $C''$ , may be called the *zincoid* (like zinc),—names which express the virtual properties of each plate, or the particular attractive power and affinity which each of them acquires from its place in the circle.

When hydrochloric acid is the polar liquid interposed between these plates, chlorine is of course attracted by the surface of the zincoid, and discharged there; and hydrogen by the face of the chloroid, and discharged upon that plate. On the electrical hypothesis, the same plates are variously denominated:—

The *zincoid* as the positive pole, the positive electrode, the anode, and the zincode.

The *chloroid* as the negative pole, the negative electrode, the cathode, and the platinode.

The cell of decomposition thus interpolated in the voltaic circle is an obstacle to induction, and reacts on the whole series, reducing the chemical action and evolution of hydrogen in each of the active cells



by at least one-third. In that retarding cell itself, the amount of decomposition is necessarily the same as in the other cells. Mr. Daniell found the chemical action reduced to one-tenth in a series of eight active and two such retarding cells; and entirely stopped by three retarding to seven active cells.

#### OF THE SOLID ELEMENTS OF THE VOLTAIC CIRCLE.

The elements of a Voltaic Circle are obviously of two different kinds—the metals or solid portions, through the substance of which chemical induction is propagated without decomposition; and the liquids in the cells, which yield to the induction and suffer decomposition. In reference to the first, it is to be observed that, as only iron and one or two other metals of the same natural family are susceptible of magnetic polarity, so the susceptibility of chemical polarity which appears in the voltaic battery is not possessed by solids in general, but is confined to the class of bodies to which zinc belongs,—the metals, all of which possess it, with the addition of carbon in the form of charcoal, and certain metallic sulphides, more particularly the sulphide of silver when heated. Weak solutions of the alkaline sulphides, containing an excess of sulphur, also admit of a feeble polarity without undergoing decomposition. The non-metallic elements, with their compounds, the oxides and salts of the metals, are destitute of this power, and cannot, therefore, be used as solid elements of the circle. A body available for this purpose is termed a *conductor* on the electrical hypothesis, a name which may be retained as it is not at variance with the function assigned to the metals in the circle viewed as a chemico-polar arrangement. Two different metals are combined in a circle, one of which is acted on by the liquid, and, therefore, called the active or the positive metal; while the other is not acted upon, and is, therefore, called the inactive or the negative metal; and it has already been stated, that the more easily acted on by the liquid, or the more highly positive the one metal, and the less easily acted upon, or more negative the other metal, the more proper and efficacious is the combination. In the following table several of the metals are arranged in the order in which they appear positive or negative to each other, when acted on by the acid fluids commonly employed in the voltaic battery. Each metal is positive to any one below it in the table, and negative to any one above it.

*Most positive.*

Potassium.

Sodium.

Manganese.

Zinc.

Cadmium.

Iron.

Nickel.

Cobalt.

Lead.

Tin.

Bismuth.

Copper.

Silver.

Mercury.

Palladium.

Carbon.

Platinum.

Rhodium.

Iridium.

Gold.

*Most negative.*

Zinc, which stands high in the list, is the only metal which can be used with advantage in the voltaic battery, as the positive metal. Although closely approaching zinc in the strength of its affinities, iron is ill adapted for the purpose, from the impossibility of amalgamating its surface, the irregularity of its structure, and certain peculiarities of this metal in reference to chemico-polarity. Platinum forms an excellent negative metal, from the weakness of its affinities, and is generally used for the plates in the cell of decomposition. Silver also is highly negative, but copper is the only negative metal which from its cheapness can be used in the construction of active cells of considerable magnitude.

*Voltaic protection of metals.*—But although the difference between two metals in point of affinity be very small, yet their association in the same acid always gives a decided predominance to the affinity of the more positive, by causing the surface of the other to become chlorous, and therefore wholly inactive in an acid fluid. A negative metal may thus be protected from the solvent action of

*on board  
or in a diagram*

saline and acid liquids, by association with a more positive metal; iron, for instance, by zinc, as in articles of *galvanized iron*, which are coated with the former metal. The process is analogous to the making of tin-plate. The surface of the iron (generally sheet iron) is first cleaned from all adhering oxide by a dilute acid: then immersed in a weak solution of tin, with fragments of metallic tin, according to the improved practice of Messrs. Morewood and Rogers, by which the iron is covered by a film of tin, to which zinc is capable of adhering more uniformly than to an iron surface. The article so prepared is then passed once through a bath of melted zinc, of which the surface is covered by the fused chloride of zinc and ammonium, to protect the metal from oxidation. It thus acquires a smooth and beautifully crystallized coating of zinc. Copper is protected by either zinc or iron, as was remarkably illustrated in the attempt made by Sir H. Davy to defend the copper sheathing of ships from corrosion in sea-water, by means of his *protectors*. These were small masses of iron or zinc fixed upon the ship's copper, at different points under the water line. They completely answered the purpose of protecting the copper, but unfortunately gave rise to a deposition of earthy matter upon that metal to which barnacles and sea-weeds attached themselves, and thereby diminished the facility of the ship's motion through the water. The more recent substitution, by Mr. Muntz, of an alloy of 60 parts of copper and 40 of zinc, for pure copper, has proved more successful. In acting as a protecting positive metal, zinc necessarily undergoes corrosion, but more slowly than might be expected. On zinced articles which are exposed to the air only, and not immersed in water, a film of suboxide of zinc soon appears, which forms a hard covering, and protects the metal below from further change.

On the other hand, the injurious effect of association with a *negative* metal is often accidentally illustrated, as in the corrosion of the ends of iron railings, which are fixed in their sockets by lead, a more negative metal. In dye-coppers, an iron steam-pipe with a rose of lead or copper is quickly destroyed. Some kinds of cast iron undergo a rapid corrosion, when exposed to sea-water, the carbon acting as a negative body and ultimately remaining in the form of plumbago after all the metal has disappeared.

A weak voltaic circle may even be formed of a single positive metal in an acid, as the zinc A B (fig. 77), provided the surfaces of the metal exposed to the acid at A and B are in different conditions as to purity or mechanical structure, and therefore unequally acted upon by the acid; whereupon the part least disposed to dissolve becomes

Spec

Spec of Metals  
Batteries.

a?

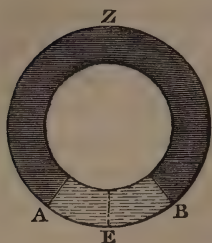
Spec

Zn + Cu

Action

Purification  
a Specimen

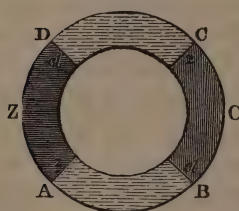
FIG. 77.



negative to the other. A zinc plate may also be unequally acted on and thrown into a polar state, from the liquid in which it is immersed varying in composition and activity at different points of the metallic surface. A circle may thus be formed of one metal A Z B, with two liquids A E and E B, which merge into each other, and form together one polar element A B.

The two metals in a circle have generally been exhibited in metallic contact, and forming together one polar element, but they may be separated, as are the zinc and copper plates A D and C B in the diagram (fig. 78), by two fluids, provided these fluids are such as a

FIG. 78.



strong acid at A B, and as iodide of potassium at D C, the first of which acts very powerfully on zinc, while the other acts very feebly upon that metal (unless associated with copper); so that of the consequent opposing inductions, that originating at A greatly exceeds and overpowers that of D. It is likewise necessary that the fluid D C be of easy decomposition, so as to yield to

the polar power of the single circle. In this arrangement, however, it is obvious that the zinc itself forms a complete polar segment, of which A is the zincous, and D the chlorous pole; and the copper also an entire polar segment of which B is the chlorous, and C the zincous pole.

The preceding table exhibits the relation which the metals enumerated assume to each other, in the acid and saline solutions usually employed as exciting fluids. But the relation of any one metal to another is not the same in all exciting fluids. Thus when tin and copper are placed in acid solutions, the former is most rapidly corroded and becomes the positive metal, according to its position in the series, but if they are put into a solution of ammonia which acts most upon the copper, then the latter becomes the positive metal. Copper is positive to lead in strong nitric acid, which oxidizes the former most freely, whereas in dilute nitric acid, by which the lead is most rapidly dissolved, the lead is positive.

#### LIQUID ELEMENTS OF THE VOLTAIC CIRCLE.

With the view of simplifying the statement of the circular decompositions which occur in the voltaic circle, the exciting fluid has



hitherto always been supposed to be hydrochloric acid (chloride of hydrogen), and this compound is a fair type of the class of bodies which possess a polar molecule, and are available for the purpose of bringing these changes into play. The exciting fluid is always a *saline body* in the general sense; that is, a binary compound of a salt-radical or halogen, such as chlorine, with a basyl, such as hydrogen or a metal. The chloride of copper, chloride of sodium, chloride of ammonium, or the chloride of any other basyl, may be substituted for hydrochloric acid, although not all with the same advantage; and the chlorides of basyls may be replaced by their iodides, sulphionides, (sulphates) nitrationsides, (nitrates) and salts of other acids, as exciting fluids, provided they have the condition of liquidity, which gives mobility to their particles, and permits that disposition of them which is assumed in a polar chain. The liquids which yield in the cell of decomposition are of the same nature, possessing always a binary polar molecule, although the liquid which forms the best exciting fluid is not always the most easily decomposed in the decomposing cell.

The positive metal which is exposed to the exciting fluid always acts in one way, displacing the basyl and combining with the halogen of that body; in the manner the zinc has been seen to liberate hydrogen and combine with chlorine, when hydrochloric acid is the exciting fluid. The positive metal is thus substituted for a similar basyl in a pre-existing saline compound. That metal may dissolve in another manner, by uniting directly, for instance, with free chlorine or iodine in solution, but then no polar chain is formed. Particles of chlorine may extend from the zinc to the associated negative metal, but not possessing a binary molecule they have no occasion to throw themselves into a polar chain in order to act upon the zinc, as the molecules of hydrochloric acid require to do in the same circumstances. The particles of these free elements appear to be incapable of that polar condition, having chlorous affinity on one side and zincous on the other, of which both the solid and liquid constituents of the voltaic circle must be susceptible. Judging from the uniformity in composition of exciting liquids, their capacity to form polar chains depends on their consisting of an atom of basyl and an atom of salt-radical, which are respectively the locus of zincous and chlorous affinity or polarity. Such molecules may be looked upon as in a state of tension when forming a part of a polar chain, each about to divide into its chlorous and zincous atoms. Mr. Faraday had established that all exciting liquids are binary compounds of single equivalents of salt-radical and basyl, or *proto-compounds*, such as hydrochloric acid itself, proto-chloride of tin, &c. Other

saline bodies which are *per-compounds*, such as bichloride of tin, are not exciting or polar, because, as may be supposed, they are not naturally resolvable into a chlorous and zincous atom, but into a chlorous atom and *another salt*; the bichloride of tin, for instance, into chlorine and proto-chloride of tin. Certain compounds, which are deficient in the saline character and not polarizable, such as chloride of sulphur, and the liquid chlorides of phosphorus and carbon, have been enumerated as exceptions to this rule. None of these bodies, however, is really a proto-compound.

The zinc or positive metal, too, always forms a proto-compound in dissolving, which is a saline body. The order of the chemical changes in the exciting fluid therefore is as follows:—The zinc in decomposing a binary compound and forming a binary compound liberates an atom of its own class; which atom repeats the same actions; supplying at the same time another atom of the same kind to act in the same manner, and that another, from the zinc to the copper plate. The combining bodies are always a basyl and a salt-radical, and therefore only two kinds of attraction or affinity are at work throughout the chain, those of a basyl and a salt-radical, the zincous and chlorous affinities. Hence, in the present subject of chemical polarity, we have to deal with but two attractive forces, the zincous and the chlorous, as in magnetism with but two magnetic forces, the austral and the boreal.

On the electrical hypothesis, a body which is thus decomposed in the active cells, or in the cell of decomposition, is called an *electrolyte* (decomposable by electricity), and this kind of decomposition is distinguished as *electrolysis*. The two elements of an electrolyte, which travel or are transferred in opposite directions, in its decomposition have been named *ions* (from *ἰων*, going); the halogen which travels to the positive metal or terminal, the *anion* (going upwards), and the basyl, which is transferred to the negative metal, or terminal, the *cation* (going downwards). Strictly chemical expressions equivalent to the former would be *zincolyte* and *zincolysis*, the decompositions throughout the circle being referred to the affinity of zinc or the positive metal.

The characters of the two constituents of an electrolyte may be shortly noticed. The class of basyl constituents is composed of the metals in their order as positive metals, beginning with potassium, and terminating with mercury, platinum, and the less oxidable metals. Ammonium has a claim to be introduced high in this list, and should probably be accompanied by the analogous basyl of the aniline class of bases and of the vegeto-alkalies, although in respect

to the decomposition of their salts in the voltaic circle, we have little precise information. Hydrogen likewise finds a place near copper in this class.

At the head of the halogen constituents of electrolytes may be placed iodine and the other members of the chlorine family. These are followed by the halogens of the sulphates, nitrates, carbonates, acetates, and other oxygen-acid salts. Sulphur must be allowed to follow the last, as the salt-radical of the soluble sulphides, and the lowest place be assigned to oxygen, as the salt-radical of the soluble metallic oxides; of oxide of potassium, for instance, and of water. It is unusual to speak of oxygen as a salt-radical, and of caustic potash and water as salts, but the binary theory of salts recognizes no essential difference between the chloride, sulphionide, and oxide of a basyl, the oxide being connected with the more highly saline compounds through the sulphide, and the list of salt-radicals forming a continuous descending series from iodine to oxygen.

The facility of decomposition of different electrolytes appears to depend more upon the high place of their salt radical, than upon the nature of their other constituent. The iodides, for instance, as iodide of potassium and hydriodic acid, are the most easily decomposed of all salts, yielding to the polar influence of the single circle. Then follow the chlorides,—chloride of lead, fused by heat, yielding to a very moderate power. After these the salts of strong oxygen acids, such as sulphates and nitrates either of strong bases, such as potash and soda, or of weak bases, such as oxide of copper and water (the hydrated acids are such salts). The carbonates and acetates, which have much weaker salt-radicals, are still less easily decomposed, and finally oxides are decomposed with great difficulty. Water itself is polarized with such extreme difficulty, and decomposed when alone to so minute a degree, even by a powerful battery, as long to have left its claim uncertain to be considered an electrolyte, when in a state of purity.

Widely as the more characteristic halogens and basyls differ, still the classes pass by imperceptible gradations into each other, and form portions of one great circular series. Mercury and the more negative metals, although clearly basyls, appear at times to assume the salt-radical relation to the highly positive metals; such a character is evinced in mercury, by the energy with which it unites with sodium and potassium, and by its function in the amalgamated zinc plate of the voltaic circle. So that the salt-radical or basyl character of a body is not absolute, but always relative to certain other bodies.



The addition of a salt or acid, even in minute quantity, to water in the cell of decomposition, causes the copious evolution of oxygen and hydrogen gases at the zincoïd and chloroid, and is therefore often spoken of as facilitating, by its presence, the decomposition of the water, in some way which cannot be explained. But the phenomena are unattended with difficulty on the binary theory of saline bodies. When sulphate of soda exists in the water of the decomposing cell, it may be sulphionide of sodium which is decomposed,  $\text{SO}_4$ , the sulphate radical being evolved at the zincoïd, and sodium at the chloroid. But the sodium having a strong affinity for oxygen reacts upon the water at the pole, forming soda and liberating hydrogen, which therefore appear together; while  $\text{SO}_4$  having, as a high salt-radical, a powerful affinity for hydrogen, likewise decomposes water, and thus evolves oxygen, which, with a free acid, appears at the zincoïd. A solution of chloride of sodium is decomposed in the same manner, its elements chlorine and sodium being attracted to the zincoïd and chloroid respectively, but neither of these elements appearing as such. Both decompose water, and thus produce oxygen with hydrochloric acid at the zincoïd, and soda with hydrogen at the chloroid. It has indeed been ascertained that the polar influence which apparently effects two decompositions in these circumstances, namely, that of water into oxygen and hydrogen, and of a salt into its acid and alkali, is no more in quantity than is necessary to decompose one of these bodies, the circulating power being measured by the quantity of fused chloride of lead decomposed in another part of the circuit (Daniell). There can be little doubt, then, that only one binary compound is immediately decomposed, and that the two sets of products which appear at the terminals are the results of secondary decomposition. Indeed, the decomposition of salts in the voltaic circle is supposed to afford considerable support to the salt-radical theory of these bodies (page 186).

Certain salts form a polar chain, or conduct, without undergoing decomposition, in a way which cannot at present be explained, particularly the iodide of mercury and fluoride of lead, both fused by heat. According to recent observations of M. Matteucci many other fused salts conduct to a greater extent than is indicated by their decomposition.

*Secondary decompositions.*—The products of voltaic action are frequently of the secondary character just described, the original products being lost from their reaction upon the liquid in which they are produced, or upon the substance of the metallic terminals. Thus, salts of the vegetable acids often afford carbonic acid, and salts of

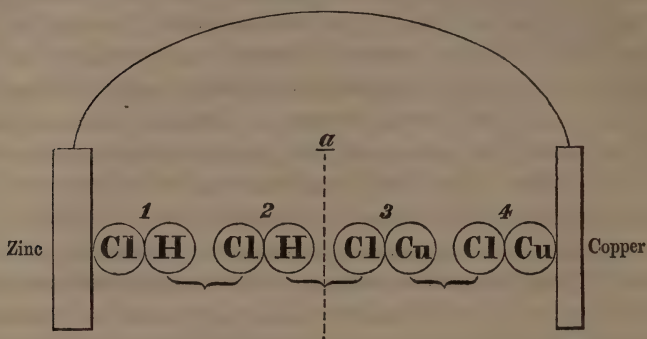


ammonia nitrogen, instead of oxygen, at the positive terminal or zincoïd; the oxygen liberated having reacted upon the combustible constituents of these bodies. Nitrates, again, may afford nitrogen, or nitric oxide, at the negative terminal or chloroïd, in consequence of the oxidation of the hydrogen evolved there. The nascent condition of the liberated elements favours such secondary actions. When the zincoïd is composed of a positive metal, such as zinc itself or copper, the chlorous element is absorbed there, combining with the metal. The decomposition of a salt is also then much easier, the action of the circle being greatly assisted by the proper affinity of the matter of the zincoïd for a chlorous body. Indeed, when two pieces of the same metal communicate by means of one of its salts, the phenomena are the same as if the metallic circuit were complete (Faraday). Insoluble sulphides, chlorides, and other compounds of a positive metal acting as the zincoïd, have thus been slowly produced in a single circle with a weak exciting fluid; which product shew exhibited distinct crystalline forms, resembling natural minerals, not otherwise producible by art. The hydrogen evolved upon a platinum chloroïd, immersed in the solution of a copper or iron salt, may also reduce these metals upon the surface of the platinum, in the form of brilliant octahedral crystals. In the active cells themselves a secondary decomposition is apt to occur, the hydrogen evolved decomposing the salt of zinc which accumulates in the liquid, and occasioning a deposition of that metal upon the copper plate; an occurrence which may determine an opposite polarity, and cause the action of the circle to decline. But on disconnecting the zinc and copper plates, the foreign deposit upon the latter is quickly dissolved off by the acid. The inconvenience of this secondary decomposition in the exciting cells is avoided by dividing the cell into two compartments, by a porous plate of earthenware interposed between the zinc and copper plates. The salt of zinc formed about that metal is prevented from diffusing to the copper, by the diaphragm, although it allows, from its porosity, a continuity of liquid polar molecules between the metals.

*Two polar liquids separated by a porous diaphragm.*—The liquids on either side of the porous division may also be different, provided they have both a polar molecule. Thus, in fig. 79, the polar chain is composed of molecules of hydrochloric acid, extending from the zinc to the porous division at *a*; and of molecules of chloride of copper, from *a* to the copper plate. When the Cl of molecule 1 unites with zinc, the H of that molecule unites with the Cl of molecule 2 (as indicated by the connecting bracket below), the H of molecule 2 with

the Cl of molecule 3, the Cu of molecule 3 with the Cl of molecule 4, and the Cu of this molecule, being the last in the chain, is deposited

FIG. 79.



upon the copper plate. Dilute sulphuric acid, in contact with an amalgamated zinc plate, and the same acid fluid saturated with sulphate of copper, in contact with the copper plate, are a combination of fluids of most frequent application. In such an arrangement, the formation of small gas bubbles upon the negative plate, which makes its contact with the acid fluid imperfect, is avoided; and the surface of that plate is kept clean and entirely metallic by the constant deposition of fresh copper upon it. The copper is deposited in a coherent state, and forms a plate, which may be stripped off from the original copper after attaining any desired degree of thickness,—and presents an exact impression of the surface of the latter. In the operation of *electrotyping*, the article to be copied is so placed in a copper solution as the negative plate of a voltaic pair, being first made conducting, if not metallic and already so, by rubbing its surface over with fine plumbago. With a negative plate of platinum, undiluted nitric acid may be used in the place of the acid solution of copper in the last arrangement, with oil of vitriol, diluted with four or five times its bulk of water, about a positive plate of amalgamated zinc. The polar molecules will be, on the binary theory of salts,  $\text{NO}_6 + \text{H}$ , in the former, and  $\text{SO}_4 + \text{H}$ , in the latter fluid. The hydrogen is also here entirely suppressed at the negative plate, uniting with the fifth equivalent of oxygen in nitric acid to form water, which is attended with the evolution of peroxide of nitrogen,  $\text{NO}_4$ . The solution of the zinc, with such an arrangement of fluids, appears to give the most intense polarization that can be attained.

*Application of the voltaic circle to chemical synthesis.—*

The liquid in the decomposition cell may be divided by a porous diaphragm placed between the platinum plates, which form the zincoid and the chloroid in a similar manner, and the synthetical results of the voltaic action be had more readily apart from each other. With a solution of chlorate of potash between the plates, it is found that the oxygen, instead of being evolved at the positive pole as gas, is communicated to the chlorate of potash there, and converts it into perchlorate (Berzelius). In a solution of chloride of potassium, even when rendered acid by sulphuric acid, chlorate, and afterwards perchlorate of potash were found at the positive pole (Kolbe). A concentrated solution of chloride of ammonium evolves hydrogen at the negative pole; but neither oxygen nor chlorine at the positive pole. But the surface of the platinum plate representing the latter pole is covered with small, yellow, oily drops of chloride of nitrogen, which, as soon as the two poles are brought into contact, decompose with explosion (Kolbe). A solution of the yellow prussiate of potash is converted into the red prussiate by the action of the oxygen at the positive pole (Smee). Dr. Kolbe oxidized the cyanide of potassium in the same manner, and converted it into cyanate of potash, but did not succeed in obtaining a percyanate: nor did he succeed in forming a fluorate of potash from the fluoride of potassium by the same means.\* The decomposition of a concentrated neutral solution of valerianate of potash in the cold gave a gaseous carbo-hydrogen,  $C_8 H_8$ , of double the density of olefiant gas, and what appeared to be a new ether, containing  $C_2 H_2$  less than amylic ether. Such transformations from the series of one alcohol to that of another are of great importance, and the attaining them by voltaic action highly interesting. Six pairs of Bunsen's carbo-zinc battery were employed in these decompositions, and the action continued for several days.†

*Transference of the ions.*—With a double diaphragm cell, in which the liquid between the poles was divided into three portions, Messrs. Daniell and Miller were enabled to make some singular observations on the transfer of the ions and their accumulation at the poles. With a neutral salt of the potassium family (such as sulphate of soda), for one equivalent of salt decomposed, half an equivalent of free acid is added to the division of the cell containing the positive pole, and half an equivalent of free alkali to the division containing the negative pole—the

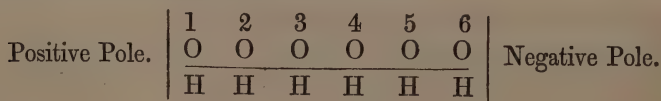
\* Memoirs of the Chemical Society, vol. iii. p. 287.

† Kolbe, *ibid.* p. 378.

amount of transference which the polar decomposition requires : but, with a salt of the magnesian family (such as sulphate of zinc), while the acid travels as usual to the positive pole and accumulates there, no corresponding transference of oxide of zinc takes place in the opposite direction. This seems to imply that water travels, as base, instead of oxide of zinc. All the magnesian salts retain one equivalent of water very strongly ; and, in the polar chain, probably assume this water as their base, so as to become equivalent to hydrated acids in solution. *The metallic oxide being transferred to an adjoining atom of salt, to form a sub salt, instead of water.* In the decomposition of salts of oxide of ammonium, the ammonia also appears passive, and does not move towards the negative pole, although the acid of the salt travels as usual towards the positive pole. The water, which is essential to the salts of oxide of ammonium, appears to be here again the base which travels ; and in a polar chain extending through a salt of ammonia, such as the sulphate of ammonia, we have probably sulphate of water as the polar molecule ; the ions being  $\text{SO}_4$  and  $\text{H}$  ; not  $\text{SO}_4$  and  $\text{NH}_4$ .\*

*Voltaic endosmose.*—It was first observed by Mr. Porrett, that in the decomposition cell, divided into two chambers by a permeable diaphragm of wet bladder or porous earthenware, the liquid tends to pass from the chamber containing the positive terminal plate into that containing the negative terminal, so as to rise at times several inches in the latter above its level in the former (Annals of Philosophy, 1816). This accumulation of liquid at the negative pole is only considerable with liquids of an inferior conducting power, that is, of difficult decomposition, and is greatest in pure water.

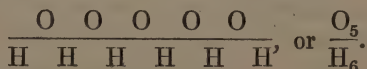
The transfer takes place of a large quantity of water with the hydrogen to the negative pole, as if the ions were  $\text{O}$  on the one side, and  $\text{H} + \text{Water}$  on the other. In a polar molecule, such as this implies, we must have an aggregation of many atoms of water forming one compound polar atom. Let us suppose six atoms of water associated  $\text{H}_6 \text{O}_6$  ; the polar molecule will be  $\text{H}_6 \text{O}_5 + \text{O}$ , in which  $\text{H}_6 \text{O}_5$  is the basyl, and  $\text{O}$  the salt-radical. Taking advantage of the graphical representation of such a compound molecule by a polar formula (page 204), in which the letters exhibit the relative position of the constituent atoms, we have—



\* Professors Daniell and Miller, "On the Electrolysis of Secondary Compounds," in the Philosophical Transactions, 1844.



The oxygen 1 is alone attracted by the positive metal or pole with which it is in contact, while hydrogen (1) being so far relieved from the attraction of its own oxygen, comes under the influence of oxygen 2, 3, 4, 5, and 6. As the salt-radical O (1) separates we have thus the temporary formation of the basylous atom—



But instead of involving six atoms of water, as in this illustration, the compound polar molecule may embrace hundreds or thousands. It will always be represented by  $\text{H}_n \text{O}_{n-1} + \text{O}$ ;  $\text{H}_n \text{O}_{n-1}$  being the basylous atom which is transferred to the negative pole, and O the salt-radical atom which is transferred to the positive pole. It appears to be by a polarization of this sort that, in bad conductors, mass compensates for conducting power; as in the return current of the electric telegraph through the earth, where the resistance is found to be even less than in the metallic wires; indeed, quite inappreciable.

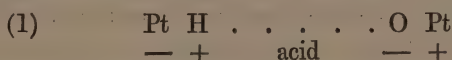
It is found by Mr. J. Napier that the passage of a salt without decomposition, such as sulphate of copper, from the positive to the negative division of the decomposition cell, may take place independently of the water in which it is dissolved, and to a greater proportional amount (Mem. Chem. Soc. ii. 28). This unequal movement of the salt and water proves that the phenomenon is not simply a flowing of the liquid towards the negative pole; and it allows us to suppose that an aggregate polar molecule may be formed of many atoms of a salt, as well as of water. It is only in dilute saline solutions that the voltaic endosmose is perceptible.

#### VOLTAIC CIRCLES WITHOUT A POSITIVE METAL.

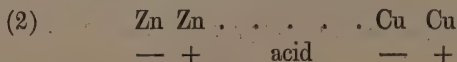
If we dip together into an acid fluid two platinum plates, one clean, and the other coated with a film of zinc or highly positive metal, we have the speedy solution of the positive metal by the usual polar decomposition, and hydrogen transferred to the opposite platinum plate. It appears that hydrogen, sulphur, phosphorus, and various other oxidable substances, will originate a polar decomposition in water or a saline fluid, when associated with platinum, in the same manner as the zinc is in the last experiment; and circles may thus be formed without a positive metal. The non-metallic but oxidable ele-

ments enumerated cannot be substituted in mass for zinc or the positive metal, because they are non-conductors; but in the thinnest films they are not so, if we may judge from experiments of this kind, and become quite equivalent to metals. Farther, with chlorine or any other strongly halogenous element dissolved in water, and placed in contact with one of the platinum plates, while the other is clean, we may have a polarization originating with the chlorine, and causing the transfer of the oxygen or salt-radical of the interposed water, or saline fluid, to the clean platinum. Nothing like this is witnessed in the voltaic combination of two metals; it is equivalent to an action in which the copper or negative metal originated the polarization by its affinity for the hydrogen or basylous constituent of the polar liquid.

1. With hydrogen gas dissolved in the acid fluid of one chamber of the divided cell, and air or oxygen in the other, polarization occurs on uniting the platinum plates, attended with the oxidation of the hydrogen and disappearance of both gases (Schönbein). Viewing this arrangement as a simple circle, consisting of a liquid and metallic segment (page 245), we have to consider particularly the composition of the terminal polar molecules at either end of the metallic segment—platinum with hydrogen must form the one at the positive pole, and platinum with oxygen the other at the negative pole:—



These are equivalent to the external molecules of the two metals, zinc and copper, in the usual voltaic arrangement, which are composed in that case of two atoms of zinc on the one side, and two atoms of copper on the other (fig. 68, page 245):—

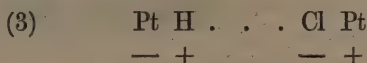


The peculiar superiority of platinum, as the single metal, in arrangements of the present class, depends upon its strictly intermediate character between basyls and halogens, so that it lends itself to form a polar binary molecule equally with hydrogen or oxygen in (1),—with both basyl and salt-radical.

The intermediate liquid (the acid) must be a binary compound as usual. Here the positive hydrogen combines with the salt-radical of that binary compound, and sends its hydrogen or basyl to the second or opposite plate; while the oxygen at that plate decomposes the

binary liquid also, sending back oxygen or salt-radical to the hydrogen of the first plate. There are, therefore, two concurring polarizations in every polar chain, tending to bring about simultaneously the same combinations and decompositions throughout the circle: hydrogen enters into combination on the one side, and oxygen on the other, in one and the same polar chain. The union of concurring primary zincous and chlorous polarizations, exhibited in such an arrangement, offers a new means of increasing polar intensity, entirely different from the multiplication of couples in the compound circle, of which the application will be fully observed afterwards in the nitric acid battery of Mr. Grove. The temporary combination of hydrogen with copper, the former as the basylous and the latter as the halogenous element of one polar molecule, which it is necessary to assume in explaining the circular polarity of the ordinary voltaic circle (page 246), is quite in accordance with the relation of hydrogen to platinum in the present circles.

2. A circle of still higher power is formed with chlorine gas, dissolved in the negative chamber, against hydrogen in the positive chamber of the divided cell. Here the terminal polar molecules of the metallic segment are:—



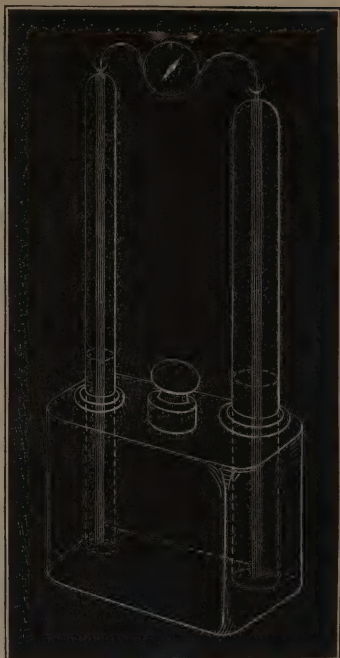
3. *Inflammation of mixed hydrogen and oxygen by platinum.*—There is every reason to believe that the remarkable action of clean platinum, both in the form of a plate and of platinum sponge, in disposing a mixture of oxygen and hydrogen in the gaseous state to unite, is the same in nature as its action upon these elements liquefied and in solution in water. In the former, as in the latter case, a polar chain must arrange itself in the platinum mass, of which one terminal molecule is platinide of hydrogen, and the other oxide of platinum (3). A less certain point is, whether the chain is completed by the interposition of a binary molecule of water already formed, between the polar H and O; or these atoms come immediately into contact, and close the circle, without the intervention of any compound polar molecule.

4. *Gas-battery.*—The gas-battery of Mr. Grove belongs to this class of voltaic arrangements. It is essentially an apparatus in which a supply of both negative and positive gas is kept over the liquid at each plate, to supply loss by absorption. A simple circle consists of a bottle (fig 80.) containing a dilute acid, with two tubes filled with oxygen and hydrogen respectively, and placed in two open-

ings in the bottle. The platinum plates contained in these tubes are made rough by adhering reduced spongy platinum, which enables them also to retain the better on their surface a portion of the acid fluid into which they dip. The two plates are connected by a wire above the tubes, which is represented in the figure as carried round a magnetic needle, to obtain evidence of polarization in the wire. Here, as in (2), the gases only act when in contact with the platinum surface and taking a part in the terminal polar molecule, and also when covered by liquid, which is necessary to complete the polar chain between the terminal polar molecules on each side. The gases in the tubes are supplementary, and do not take a part in the polar chain. The modifications of this battery, where, instead of hydrogen gas, sulphur or phosphorus, vaporized in nitrogen gas, or a gaseous hydro-carbon, is placed at the positive pole, are of the same character, and only act by supplying a film of an oxidable body, such as sulphur, or phosphorus, to the surface of the platinum, capable of forming the positive element of a polar molecule with that metal. This, again, must be covered by the binary acid fluid, in order to communicate by a polar chain with the oxygen of the terminal molecule of platinum and oxygen in the negative chamber of the divided cell.\*

5. Closely resembling these circles is that in which one of the platinum plates is covered by a film of peroxide of lead or peroxide of manganese. The platinum plate may be so prepared by making it the negative terminal for a short time in a solution of acetate of lead or of protosulphate of manganese. In an acid fluid, which is capable of dissolving the protoxide of lead or manganese, polarization occurs, the excess of oxygen of the attached peroxide forming with

FIG. 80.

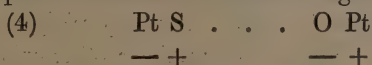


\* Grove, On the Gas Voltaic Battery: Philosophical Transactions, 1843 and 1845.

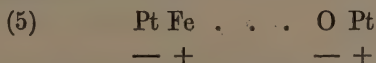


platinum a polar molecule, in which the oxygen is the chlorous element. This decomposes the saline molecule of the acid, or water, causing the transference of the salt-radical or oxygen to the clean platinum plate, where it may be evolved as gas. This most nearly resembles the case with chlorine—water at one platinum plate, which causes the evolution of oxygen at the other platinum plate; the only source of polarizing power in the circle being a chlorous affinity.

6. By much the most powerful voltaic arrangement of this class is that in which one chamber of the divided cell is charged with a solution of sulphide of potassium, and the other chamber with strong nitric acid.\* Here we have two concurring sources of polarization in one polar chain, namely, the affinity of sulphur for oxygen, tending to transmit hydrogen in one direction, and the easy decomposition of nitric acid into  $\text{N O}_4$  and  $\text{O}$ , supplying oxygen to the surface of the platinum, which sends a chlorous element in the opposite direction. The terminal polar molecules of the metallic segment of the circle are—



With a single pair of plates so charged water may be decomposed. The action is equally powerful with chlorine substituted for the nitric acid. Such combinations of fluids may be greatly varied: all that is necessary is an oxidable substance at one plate, and an oxidizing substance at the other. In the first class are protosalts of iron, tin and manganese, sulphides, sulphites, hyposulphites; in the second, chlorine, nitric, chromic and manganic acids, and persalts of iron and tin. Taking protoxide of iron against peroxide as an example of these cases, the terminal molecules of the metallic segment may be represented as—



It is true we have no evidence of the actual separation of the iron or of the oxygen upon the platinum surface; still there is reason to believe such a polarity to be established, assisted by secondary affinities; the oxygen of the protoxide of iron passing over to an adjoining double molecule of protoxide, and converting it into peroxide, to allow the metal to join in a polar molecule with the platinum. At the same time, the peroxide of iron at the negative plate may become protoxide, while its oxygen is engaged in forming a polar molecule with the platinum. But the intensity of polarization with the salts

\* Mr. A. R. Arrott, on "Some New Cases of Voltaic Action;" *Memoirs of the Chem. Soc.* i. 142.

of iron against each other is feeble compared with that of chlorine or nitric acid against an alkaline sulphide. In all these cases the polar circle must be completed by a saline compound in the liquid or liquids, which may serve as the means of connecting the terminal molecules described of the platinum plates, and by metallic polar molecules through the wire connecting the platinum plates.

It was supposed by M. Becquerel that a circle of the present description may be formed in which the affinities are those of an acid for an alkali: the acid and alkaline solutions being separated by porous baked clay, which leaves them in free liquid contact, although their actual mixture proceeds with extreme slowness. Sulphuric acid and potash, however, are generally admitted to be nearly or altogether incapable of producing this effect, while acids which part readily with oxygen, such as iodic, chloric, chromic, or nitric acid, with an alkali, produce a powerful effect. The polarization may be referred to the oxygen of the acids, in these last cases, at the negative terminal, and is a chlorous affinity. It may possibly be often assisted by minute quantities of ammonia, organic or other oxidizable matter, at the positive terminal in the alkaline solution.\*

*Theoretical considerations.*—The facility with which circular decompositions take place, and the necessity of their occurrence in the action of binary compounds, which was explained under the atomic exhibition of a double decomposition at page 239, are undoubtedly the key to the great stimulus to chemical activity, which the voltaic arrangement affords. Reverting to the original illustration of the action of hydrochloric acid upon zinc, it may be observed that zinc has a strong attraction for chlorine, and would combine at once with that element if the latter were free, without foreign aid of any kind. But with the chlorine of hydrochloric acid the case is different. That chlorine is already combined and strongly retained by its own hydrogen: to enable the chlorine to enter into a new combination we must relieve it from this attraction, by engaging otherwise the affinity of the hydrogen. The contrivance of the voltaic circle is to present another halogen to the hydrogen, and thus divert its affinity from the chlorine—the latter being thereby left free to combine with the zinc. This requires a train of similar decompositions passing round a circle to the zinc, illustrated in diagram 68 of page 245; and which ends in relieving the external combining atom of zinc from the attraction of even the contiguous atom of the

\* Becquerel, *Elements d'Electro-Chimie*, 1843.

same kind; thus dissolving the attraction of aggregation in the metal, and resigning the external atom of zinc entirely to the attraction of the equally relieved chlorine. It is entirely, therefore, because the agent applied to the zinc is a binary compound, and not a free element, that this circular mode of action is necessary.

It is to be remarked in explanation of the facility with which the mutual combinations and decompositions in a circular chain occur, that they do not necessarily consume any power or occasion waste of force. They may be compared to the movement of a nicely balanced beam on its pivot, or the oscillation of a pendulum, in which the motion is equal in two opposite directions, and requires only the minimum of effort to produce it.

Farther, it is not to be supposed that zinc dissolves by a circular action of affinity, only when a negative metal is attached to it, and a voltaic circle purposely constructed. For this positive metal never appears to dissolve in hydrochloric acid in any other manner; the formation of little polar circles in the fluid, starting from one point of the metallic mass and returning upon another, being always required for its solution (page 268). In the solution of zinc, therefore, by a binary saline body, such as hydrochloric acid, the circular or voltaic polarization is the necessary, as well as the most effective mode of action of chemical affinity.

The molecular condition of conductors, such as carbon and the metals, in a voltaic circle, appears to be that of polymeric combination. Their atoms must be feebly basylous and chlorous to each other; the distinction possibly depending upon inequality in their proportions of combined heat, and maintain the relation of combination. Again, many of these binary molecules are associated together like the many similar atoms of carbon, or of hydrogen, which we find associated in the polymeric hydrocarbons. The whole must be held together by their chemical affinities, and the aggregation of the mass be the final resultant of the same attractions. The determination of the polar condition in two metals, by the mere application of heat or cold to their junction, requires the assumption of the sali-molecular structure of metals; and the other proposition, that affinity passes into aggregation, is equally necessary to account for the polar (or electrical) effects which are produced by friction or abrasion, as they appear to extend to the division of chemical molecules.

The cumulative nature of chemical combination is well illustrated in such compounds as the acid hydrates—in dilute sulphuric acid, for instance, where we find an atom of acid uniting with more

and more atoms of water, with a decreasing affinity, but without any assignable limit to their number. It is worthy of remark that the acids are bodies with chlorous or negative atoms, and their peculiar affinity in excess. The polar formula for sulphuric acid (page 205) is  $\frac{O_3}{S}$ ; or three negative to one positive atom. By the apposition of a single binary molecule of water, sulphate of water is produced,  $\frac{O_3}{S} \frac{O}{H}$ , in which the excessive proportion of chlorous atoms and affinity in the compound is in some degree diminished, the formula of the latter presenting four negative to two positive atoms. The apposition of more and more molecules of water is determined by this excess of chlorous affinity, which it tends to neutralize; the constant difference, or excess of two chlorous over the number of basylous atoms, becoming proportionally less with large numbers of added molecules of water. All the magnesian bases appear to assume water to assist in neutralizing their acid in the same manner, and retain one equivalent of this water in general very strongly. In the formation of a polar chain through a solution of a sulphate of this class, we have had reason to suppose that the sulphuric acid applies itself, for the time, to the water rather than the metallic oxide as its base (page 265). The phenomena of voltaic endosmose were also found to favour the idea of the polarization of highly aggregated molecules, in which the binary molecule was represented by a single atom of chlorine or salt-radical, against a single atom of hydrogen or metal associated with a large number of atoms of water, which constituted together the basylous atom. The application of polar formulæ to the explanation of voltaic decompositions of all kinds would, I believe, more correctly express the molecular changes that occur, than the usual assumption of the binary division of the compound body, in an absolute manner, into a basylous atom and a fictitious group forming a halogen body.

#### GENERAL SUMMARY.

1. In a closed voltaic circle, a certain number of lines or chains of polarized molecules is established, each chain being continuous round the circle. Hence the polar condition of the circle must be every where the same. The same number of particles of exciting fluid are simultaneously polar upon the surface of every zinc plate in the active cells, and also upon the surface of the zincoïd in the cell



of decomposition, and the consequent chemical change, or decomposition occurring, is of the same amount in all the cells in the same time. This equality in condition and results is essential to a circular polarization, such as exists in the voltaic circle.

The number of polar chains that can be established at the same time in a particular voltaic arrangement, is obviously affected by several circumstances:—

(1) By the size of the zinc plate: the number of particles of zinc that may be simultaneously acted upon by the exciting fluid being directly proportional to the extent of metallic surface exposed.

(2) By the nature and accidental state of the exciting liquid, some electrolytes being more easily acted on by the positive metal than others; while the state of dilution, temperature, and other circumstances, may affect the facility of decomposition of any particular electrolyte.

(3) The adhesion of the gas bubbles of hydrogen to the copper plate, at which they are evolved, interferes much with the action of a battery; partly by reducing the surface of copper in contact with acid, and partly by acting as a zincous element, and originating an opposite polarization in the battery (page 269). By taking up the hydrogen, by means of a solution of sulphate of copper in contact with the copper plate, Mr. Daniell increased the amount of circulating force six times.

(4) The chemical action in a cell is also diminished by increasing the distance from each other in the exciting fluid of the positive and negative metals.

(5) The lines of chemico-polar molecules in the exciting fluid should be repulsive of each other, like lines of magneto-polar elements, as illustrated in the mutual repulsion and divergence of the threads of steel filings which attach themselves to the pole of a magnet (fig. 63, page 237). That the lines of induction do diverge greatly in the acid, starting from the zinc as a centre, is placed beyond doubt by many experiments of Mr. Daniell. A small ball of zinc suspended in a hollow copper globe filled with acid, is the arrangement in which this divergence is least restrained, and was found to be the most effective form of the voltaic circle. When the copper, too, is a flat plate, and wholly immersed in the acid, the back is found to act as a negative surface, as well as the face directly exposed to the zinc, showing that the lines of induction in the acid expand, and open out from each other, some bending round the edge of the copper plate and terminating their action, after a second flexure, on

its opposite side. To collect these diverging lines, the surface of the copper may be increased with advantage to at least four times that of the zinc.

(6) The polar chains of molecules, in the connecting wires and other metallic portions of the circle, must be equally repulsive of each other. Hence the small size of the negative plates in the active cells, and of the platinum plates in the cell of decomposition, and the thinness of the connecting wires, are among the circumstances which diminish the number of polar chains that can be established, and impair the general efficiency of a battery.

2. The effect of multiplying the active cells in a battery is not to increase the number of polar chains, or *quantity* of decomposition, but to increase the *intensity* of the induction in each chain; although this increase in intensity generally augments the quantity also, in an indirect manner, by overcoming more or less completely such obstacles to induction as have been enumerated.

3. The intensity of the induction, also, is much greater with some electrolytes than others. Thus a single pair of zinc and platinum plates excited by dilute sulphuric acid, decomposes iodide of potassium, proto-chloride of tin, and fused chloride of silver, but not fused nitre, chloride or iodide of lead, or solution of sulphate of soda. With the addition, however, of a little nitric acid to the sulphuric, the same single circle decomposes all these bodies, and even water itself. Here we have a primary chlorous induction from the oxygen of the nitric acid, in addition to the basylous induction of the zinc (page 268). The former action also is attended by the suppression of the hydrogen, so that the evolution of that gas upon the negative plate is avoided.

4. The division of the connecting wire, and the separation of its extremities to the most minute distance from each other, is sufficient to stop all induction and the propagation of the polar condition in an arrangement with the usual good conducting fluids. In a powerful voltaic battery consisting of seventy large Daniell cells, no induction was observed to pass when the terminal wires were separated not more than the one-thousandth of an inch, even with the flame of a spirit-lamp or rarified air between them. Absolute contact of the wires was necessary to establish the circulation. But after contact was made, and the wires were heated to whiteness, they might be separated to a small distance without the induction being interrupted: the space between them was then filled with an arch of dazzling light, containing detached particles of the wire in a state of

intense ignition, which were found to proceed from the zincoid to the chloroid,—the former losing matter, and the other acquiring it. So highly fixed a substance as platinum is carried from the one terminal to the other in this manner; but the transference of matter is most remarkable between charcoal points, which may be separated to the greatest distance, and afford the largest and most brilliant arch of flame. A similar, although it may be an excessively minute detachment of matter, is found to accompany the electric spark in all circumstances. Hence, the electric spark always contains matter. In a powerful water battery, however, of a thousand couples, where the conducting power of the liquid is low, good sparks are obtained on approaching the terminals (Gassiot).

5. When terminal wires of a voltaic circle are grasped in the hands, the circuit may be completed by the fluids of the body, provided the battery contains a considerable number of cells, and the induction is of high intensity: the nervous system is then affected, the sensation of the electric shock being experienced.

6. The conducting wire becomes heated precisely in proportion to the number of polar chains established in it, and consequently in proportion to the size of the zinc plate; and this to the same degree from the induction of a single cell as from any number of similar cells. Wires of different metals are unequally heated, according to the resistance which they offer to induction. The following numbers express the heat evolved by the same circulation in different metals, as observed by Mr. Snow Harris:—

	Heat evolved.	Resistance.
Silver . . . . .	6	1
Copper . . . . .	6	1
Gold . . . . .	9	1½
Zinc . . . . .	18	3
Platinum . . . . .	30	5
Iron . . . . .	30	5
Tin . . . . .	36	6
Lead . . . . .	72	12
Brass . . . . .	10	3

The conducting powers of the metals are inversely as these numbers; silver being a better conductor than platinum in the proportion of 5 to 1. The conducting power of all of them is found to be diminished by heat.

7. As a portion of the voltaic circle, the conducting wire acquires



extraordinary powers of another kind, which can only be very shortly referred to here, belonging as they properly do to physics.

(1) Another wire placed near and parallel to the conducting wire, has the polar condition of its molecules disturbed, and an induction propagated through it in an opposite direction to that in the conducting wire.

(2) If the conducting wire be twisted in the manner of a corkscrew so as to form a hollow spiral or helix, it will be found in that form to represent a *magnet*, one end of the helix being a north, and the other a south pole; and, if moveable, will arrange itself in the magnetic meridian, under the influence of the earth's magnetism. Its poles are attracted by the unlike poles of an ordinary magnet, and it imparts magnetism to soft iron or steel by induction. Two such helices attract and repel each other by their different poles, like two magnets. Indeed, an ordinary magnet may be viewed as a body having a helical chain of its molecules in a state of permanent chemico-polarity.

(3) If a bar of soft iron bent into the form of a horse-shoe, with a copper wire twisted spirally round it, be applied like a lifter to the poles of a permanent magnet, at the instant of the soft iron becoming a magnet by induction, the molecules of the spiral become chemico-polar; and when contact is broken with the permanent magnet, and the soft iron ceases to be a magnet, the wire exhibits a polarity the reverse of the former. By a proper arrangement, electric sparks and shocks may be obtained from the wire, while the soft iron included within it is being made and unmade a magnet. The magneto-electric machine is a contrivance for this purpose, and is now coming to supersede the old electric machine, as a source of what is termed electricity of tension. Magnetic and electric effects are thus reciprocally produced from each other.

4: (4) When the pole of a magnetic needle is placed near the conducting wire, the former neither approaches nor recedes from the latter, but exhibits a disposition to *revolve round it*. The extraordinary and beautiful phenomena of electrical rotation are exhibited in an endless variety of contrivances and experiments. As the magnetic needle is generally supported upon a pivot, it is free to move only in a horizontal plane, and consequently when the conducting wire is held over or under it (the needle being supposed in the magnetic meridian), the poles in beginning to describe circles in opposite directions round the wire, proceed to move to the right and left of it, and thus deviate from the true meridian. The amount of de-

*This notion of rotation - really a molecular bending of the magnet - a tendency to assume a curved form. Compare to the bending of a substance as it cools, round the source of heat, from loss of motion on one side.*



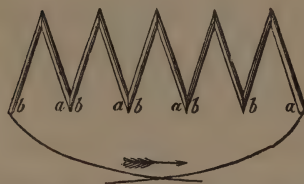
viation in degrees is proportional to the quantity of circulating induction, and may be taken to represent it, as is done in a useful instrument, the galvanometer, to be afterwards described. It was in the form of these deflections, that the phenomena exhibited by a magnet, under the influence of a conducting wire, first presented themselves to Oersted in 1819.

FIG. 81.



8. Thermo-electrical phenomena are produced from the effect of unequal temperature upon metals in contact. If heat be applied to the point *c*, (fig. 81), at which two bars of bismuth and antimony *b* and *a* are soldered together, on connecting the free extremities by a wire, the whole is found to form a weak voltaic circle, with the induction from *b* through the wire to *a*. Hence in this thermopolar arrangement the bismuth is the negative metal, and may be compared to the copper in the voltaic cell. If cold instead of heat be applied to *c*, a current also is established, but in an opposite direction to the former. Similar circuits may be formed of other metals, which may be arranged in the following order, the most powerful combination being formed of those metals which are most distant from each other in the following enumeration: bismuth, platinum, lead, tin, copper or silver, zinc, iron, antimony. When heated at their points of contact, the current proceeds through the wire from those which stand first to the last. According to Nobili, similar circuits may be formed with substances of which the conducting power is lower than that of the metals.

FIG. 82.



Several pairs of bismuth and antimony bars may be associated as in fig. 22, and the extreme bars being connected by a wire, form an arrangement resembling a compound voltaic circle. Upon heating the upper junctions, and keeping the lower ones cool, or on heating the lower ones and keeping the others cool, an induction is established in the wire, more intense than in the single pair of metals, but still very weak. The conducting wire strongly affects a needle, causing a deflection proportional to the inequality of temperature between the ends of the bars. Melloni's thermo-multiplier is a delicate instrument of this kind, which is even more sensitive to changes of temperature than the air-thermometer, and has afforded great assistance in exploring the phenomena of radiant heat (page 35).

In such a compound bar, also, unequal temperature may be produced, by making it the connecting wire of a single and weak voltaic circle; whereupon the metals become cold at their junction, if the induction is from the bismuth to the antimony, and hot at the same point if the induction is in the opposite direction. These are the converse of the preceding phenomena, in which electrical effects were produced by inequality of temperature.

9. The friction of different bodies is another source of electrical phenomena. One, at least, of the bodies rubbed together must not be a conductor, and in general two non-conductors are used. When a silk handkerchief or a piece of resin is rubbed upon glass, both are found, after separation, in a polar condition, and continue in it. The rubbing surface of the glass becomes and remains zincous, and that of the resin or silk is chlorous; and a molecular polarization is at the same time established through the whole mass of both the glass and resin, reaching to their opposite surfaces, which exhibit the other polarity. The powers thus appearing on the two rubbing surfaces, being manifestly different, were distinguished by the names of the bodies on which they are developed; that upon the glass as *vitreous* electricity (basylous affinity), and that upon the resin as *resinous* electricity (halogenous affinity).

In comparing the chemico-polarity excited by friction with that of the voltaic circle, we observe that the former is of high intensity but small in quantity, or affecting only a small number of trains of molecules. Also that the polar condition is more or less permanent, depending upon the insulation, and attended with a disturbance of the polar condition of surrounding bodies to a considerable distance, giving rise to electrical attractions and repulsions, or statical phenomena. If both the excited and vitreous resinous surfaces have a conducting metal, such as a sheet of tin-foil, applied to them, and each sheet have a wire proceeding from it, the wires and tin-foil are polarized similarly to the glass and the resin which they cover; and a saline body placed between the extremities of the wires, which are respectively a zincoid and chloroid, is polarized also, and decomposed. But the amount of decomposition, which is a true measure of the *quantity* of polar chains, is extremely minute compared with the amount of polarization in the voltaic circle. Thus, Mr. Faraday has calculated that the decomposition of one grain of water by zinc, in the active cell of the voltaic circle, produces as great an amount of polarization and decomposition in the cell of decomposition, as 950,000 charges of a large Leyden battery, of several square feet of coated surface;

an enormous quantity of power, equal to a most destructive thunder storm. The polarization from friction is therefore singularly intense, although remarkably deficient in quantity, or in the number of chains of polar molecules.

The kinds of matter susceptible of this intense polarization are so many and so various, such as glass, minerals, wood, resins, sulphur, oils, air, &c., as to make it difficult to suppose that the polar molecule is of the same chemical constitution in all of them, as it is in the electrolytes of the voltaic circle. Indeed, it must be admitted that all matter whatever may be forced into a polar condition by a most intense induction.

Electrical induction at a distance, Mr. Faraday has shewn to be always an action of contiguous particles, chains of particles of air, or some other "dielectric," extending between the excited body which is inducing, and the induced body. His investigation of this subject led to the remarkable discovery that the intensity of electric induction at a constant distance from the inducing body is not always the same, but varies in different media, the induction through a certain thickness of shell-lac, for instance, being twice as great as through the same thickness of air. Numbers may be attached to different bodies which express their relative inductive capacities :—

Specific inductive capacity of air	.	.	.	1
"	"	glass	.	1.76
"	"	shell-lac	.	2
"	"	sulphur	.	2.24

The inductive capacity of all gases is the same as that of air, and this property, it is remarkable, does not alter in these bodies with variations in their density.

10. Mr. Faraday has lately made the important discovery that a ray of polarized light, passing through a transparent liquid or solid, is deflected, and takes a spiral direction, or has a motion of rotation communicated to it by the approximation of the pole of a powerful electro or natural magnet; the pole of the latter being so placed that the ray is in the direction of the lines of attraction of the magnet. The amount of the deflection of the ray varies in different transparent bodies, and is approximatively expressed for oil of turpentine by 11.8, heavy borate of lead glass 6.0, flint-glass 2.8, rock-salt 2.2, water 1, alcohol and ether less than water (Phil. Trans. 1846).

11. Operating with electro-magnets of the highest power, Mr. Faraday has obtained results of a fundamental nature respecting the

magnetic capacity of different kinds of matter. The magnetic field being represented as in fig. 83, where N and S are the two poles, the dotted line N S connecting these poles, or line of magnetic force, is conveniently termed the axial direction, and the line  $er$ , perpendicular to the former, the equatorial direction.

FIG. 83.



When a bar of bismuth, two inches long, 0.33 inch wide, and 0.2 thick, was delicately suspended by a thread of untwisted silk, and placed between the magnets, it arranged itself in the direction of  $er$ , or equatorially. All kinds of solid, liquid, and even gaseous matter have a certain amount of tendency to place themselves, like the bismuth bar, across the axial or proper magnetic direction. This equatorial tendency is, however, overcome and negatived by the smallest proper magnetic property which bodies may possess, as this is the axial polarity, and causes the substance to set with its greatest length in the direction N S. Besides iron, nickel and cobalt, the usual magnetic metals, platinum, palladium and titanium, proved to be axial bodies. So are all the salts containing iron, nickel, or cobalt, as base. Even bottle glass is comparatively very magnetic, from the iron it contains; so is crown (window) glass, but not flint glass. The solutions of these salts are also magnetic. Crystals of the yellow ferrocyanide and red ferriecyanide of potassium are not magnetic, but set equatorially. The iron, it will be remembered, belongs to the acid in these last salts. The salts of the oxides of the following metals proved magnetic, and Mr. Faraday is disposed to infer that the metals themselves are so—manganese, cerium, chromium. Paper and many other organic and mineral substances often contain enough of iron to make them fall into the same class.

The bodies which place themselves equatorially are named *diamagnetic*. The endless list of them is also headed by metals, which appear to possess this power in different degrees of intensity according to the following order:—

## DIAMAGNETIC METALS.

Bismuth.		Cadmium.
Antimony.		Mercury.
Zinc.		Silver.
Tin.		Copper.



The other non-magnetic metals are diamagnetic in a less degree. This property is not sensibly impaired by heating the metals up to their fusing points. The property may be experimentally illustrated by pointed pieces of rock crystal, glass, phosphorus, sealing-wax, caoutchouc, wood, beef, bread, &c. (Phil. Trans. 1846).

Hot air and flame are more diamagnetic than cold or cooler air, so that a stream of the former spreads itself equatorially in ascending between magnetic poles. Of many gases and vapours tried by Mr. Faraday, oxygen was found to be the least diamagnetic; and this element appears to lower the equatorial tendency of the gases into which it enters as a constituent. Nitrogen is more highly diamagnetic than carbonic acid or hydrogen. In an atmosphere of carbonic acid gas (instead of air) between the magnetic poles, streams of hydrogen gas, coal gas, olefiant gas, muriatic acid, and ammonia, passed equatorially, and are therefore more diamagnetic. A stream of oxygen, which is so little diamagnetic, had, consequently, "the appearance of being strongly magnetic in coal gas, passing with great impetuosity to the magnetic axis, and clinging about it; and if much muriate of ammonia fume were purposely formed at the time, it was carried by the oxygen to the magnetic field with such force as to hide the ends of the magnetic poles. If, then, the magnetic action were suspended for a moment, this cloud descended by its gravity; but being quite below the poles, if the magnet were again rendered active, the oxygen cloud immediately started up and took its former place. The attraction of iron filings to a magnetic pole is not more striking than the appearance presented by the oxygen under these circumstances\*."

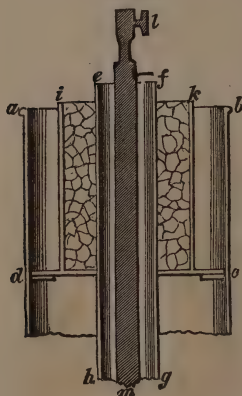
#### VOLTAIC INSTRUMENTS.

*Daniell's constant battery.*—A cell of this battery consists of a cylinder of copper  $3\frac{1}{2}$  inches in diameter, which experience has proved to the inventor to afford the most advantageous distance between the metallic surfaces, but which may vary in height from 6 to 20 inches, according to the power which it is wished to obtain. A membranous bag formed of the gullet of an ox, is hung in the centre by a collar and circular copper plate, resting upon a rim within and near the top of the cylinder; and in this is suspended by a wooden

\* Faraday, Phil. Mag. xxxi. 415.

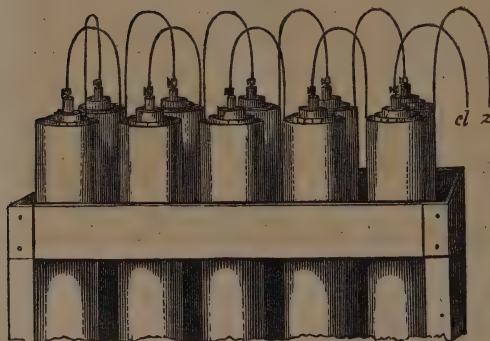
cross-bar, a cylindrical rod of amalgamated zinc half an inch in diameter. Or a tube of porous earthenware, shut at the bottom, is substituted for the membrane with great convenience. The outer cell is charged with a mixture of 8 measures of water and 1 of oil of vitriol, which has been saturated with sulphate of copper, and portions of the solid salt are placed upon the circular copper plate, which is perforated like a colander, for the purpose of keeping the solution always in a state of saturation. The internal tube is filled with the same acid mixture without the salt of copper. A section of the upper part of one of these cells is here represented: *a b c d* (fig. 84) is

FIG. 84.



the external copper cylinder; *e f g h*, the internal cylinder of earthenware, and *l m* the rod of amalgamated zinc. Upon a ledge *c d*, within an inch or two of the top of the cylinder, rests the cylindrical colander *i k*, which contains the copper salt, and both the sides and bottom of which are perforated with holes. A number of such cells may be connected into a compound circuit, with wires soldered to the copper cylinders, and fastened to the zinc by clamps and screws as shewn below, in fig. 85. (Daniell's Introduction to Chemical Philosophy).

FIG. 85.



Instead of the zinc cylinder a thick plate of laminated zinc is now generally used, which is more regularly amalgamated than the cast cylinder.

In this instrument the sulphate of zinc, formed by the solution of the zinc rod,

is retained in the stoneware cylinder, and prevented from diffusing to the copper surface; while the hydrogen, instead of being evolved as gas on the surface of the latter metal, decomposes the oxide of copper of the salt there, and occasions a deposition of metallic copper on the copper plate. Such a circle will not vary in its action for hours together, which makes it invaluable in the investigation of

voltaic laws. It owes its superiority principally to three circumstances :—to the amalgamation of the zinc, which prevents the waste of that metal by solution when the circuit is not completed ; to the non-occurrence of the precipitation of zinc upon the copper surface ; and to the complete absorption of the hydrogen at the copper surface, the adhesion of globules of gas to the metallic plates greatly diminishing, and introducing much irregularity into the action of a circle.

*Grove's nitric acid battery.*—In this battery the positive metal is amalgamated zinc, and the negative metal platinum, while the intermediate liquid is of two kinds, dilute sulphuric acid of sp. gr. 1.125 in contact with the zinc, and strong nitric acid in contact with the platinum. In fig. 86, *a* represents a flat cell of porous earthenware,

FIG. 86.



to contain the nitric acid and platinum plate ; *b*, the platinum plate ; *d*, the zinc plate, which is doubled up to include the porous cell ; *e*, a cell of glazed earthenware to contain the sulphuric acid and zinc plate ; *f*, a wooden frame to support the last cell, terminated above by copper plates provided with clamps, by which the terminal wires are attached. Two wooden wedges, such as *c*, are required to fix the upper end of the zinc plate on the one side, and the plati-

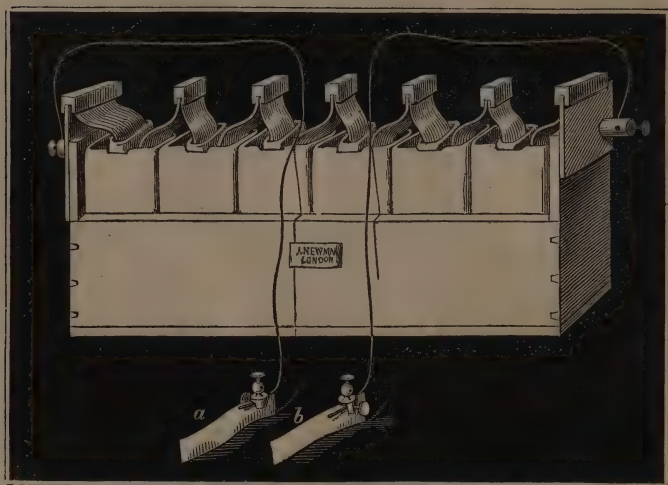
num plate on the other, as in fig. 87. Convenient dimensions for the principal parts are, the external cell *e*,  $4\frac{1}{2}$  inches by  $2\frac{3}{4}$  and  $1\frac{1}{4}$ ; porous cell *a*,  $4\frac{1}{2}$  by  $2\frac{1}{2}$  and  $\frac{3}{8}$  inch; platinum plate 5 inches by  $2\frac{1}{2}$ , and weighing about 10 grains in the square inch.

In fig. 88, six of these cells are placed together in a wooden frame, with the upper part of each end of the frame of stout sheet copper, to which the plates and wires can be clamped. The wires from the platinum and zinc ends of the battery, have platinum plates, *a* and *b*, attached to them as

FIG. 87.



FIG. 88.



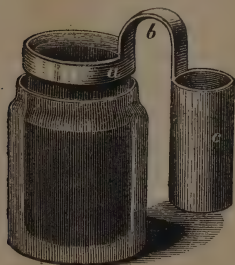
terminals. A battery of this size will evolve 8 or 10 cubic inches of mixed oxygen and hydrogen gases in the voltameter per minute. It is equal to several times as many cells of the preceding battery. The polarizing power is very intense, and little more decomposing power is gained by increasing the number of cells beyond five or six.

*The carbo-zinc battery of Bunsen*, which is much used on the continent, is a modification of the last construction, in which charcoal in contact with the nitric acid is substituted for platinum. The



carbon is in the form of a hollow cylinder, and is made by coking pounded coal in a proper iron mould. By soaking the coke in sugar, and calcining a second time, great compactness is given to the cylinder. The latter is so large as to include the porous cell containing

FIG. 89.

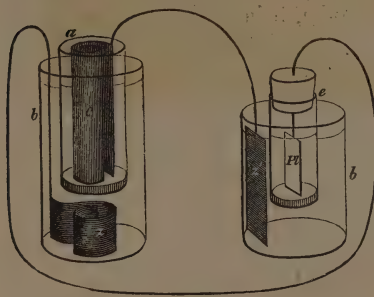


for the nitric acid.

For other useful forms of the battery, such as that introduced by Mr. Smee, in which a thin sheet of silver covered by a deposit of platinum (platinized silver) is the negative metal, I must refer to works upon Electricity.

*Bird's battery and decomposing cell.*—To M. Becquerel we are particularly indebted for the investigation of the decomposing powers of feeble currents, sustained for a long time, the results of which are of great interest, both from the nature of the substances that can be thus decomposed, and from the form in which the elements of the body decomposed are presented, the slow formation of these bodies permitting their deposition in regular crystals.\* Dr. Golding Bird has also added to the number of bodies decomposed by such means, and contrived a simple form of the battery, which, with Becquerel's decomposing cell, renders such decompositions certain and easy.†

FIG. 90.



The decomposing cell consists of a glass cylinder *a*, (fig. 90) within another glass cylinder *b*. The inner cylinder *a* is 4 inches long, and  $1\frac{1}{2}$  inch in diameter, and is closed at the lower end by a plug of plaster of Paris 0.7 inch in thickness: this cylinder is fixed by means of wedges of cork within the other, which is a plain jar, about 8

\* *Traité Experimental de l'Electricité et du Magnétisme*, par M. Becquerel.

† *Phil. Trans.* 1837, p. 37.

inches deep by 2 inches in diameter. A piece of sheet copper *c*, 4 inches long and 3 inches wide, having a copper conducting wire soldered to it, is loosely coiled up and placed in the inner cylinder with the plaster bottom: a piece of sheet zinc *z*, of equal size, is also loosely coiled, and placed in the outer cylinder; this zinc likewise being furnished with a conducting wire. The outer cylinder is then nearly filled with a weak solution of common salt, and the inner with a saturated solution of sulphate of copper. The two fluids are prevented from mixing by the plaster diaphragm, and care being taken that they are at the same level in both the cylinders, the circle will afford, on joining the wires, a continuous current for weeks, the chloride of sodium and the sulphate of copper being very slowly decomposed. After it has been in action for some weeks, chloride of zinc is found in the outer cylinder: and beautiful crystals of metallic copper, frequently mixed with the ruby suboxide (closely resembling the native copper ruby ore in appearance), with large crystals of sulphate of soda, are found adhering to the copper plate in the smaller cylinder, especially on that part where it touches the plaster diaphragm.

The decomposing cell is the counterpart of the battery itself, consisting, like it, of two glass cylinders, one within the other, the smaller one *c* having a bottom of plaster of Paris fixed into it: this smaller tube may be about  $\frac{1}{2}$  inch wide and 3 inches in length, and is intended to hold the metallic or other solution to be decomposed, the external tube *d*, in which the other is immersed, being filled with a weak solution of common salt. In the latter solution a slip of amalgamated zinc-plate *z'*, soldered to the wire coming from the copper plate *c* of the battery, is immersed; and a slip of platinum foil *pl*, connected with the wire from the zinc plate *z* of the battery, is immersed in the liquor of the smaller tube, being held in its place by a cork, through which its wire passes. The whole arrangement is now obviously a pair of active cells, of which *c z'* is one metallic element, and *z pl* the other; and the fluid between *z* and *c* divided by the porous plaster diaphragm, one fluid element, and the fluid between *z* and *pl*, divided by a porous plaster diaphragm, another fluid element; although it will be convenient to speak of the last as the cell of decomposition. With a solution of chlorides or nitrates of iron, copper, tin, zinc, bismuth, antimony, lead or silver, in the smaller tube, Dr. Bird finds the metals to be reduced upon the surface of the platinum, generally but not invariably in possession of a perfect metallic lustre, always more or less crystalline, and often very beau-

tifully so. The crystals of copper rival in hardness and malleability the finest specimens of native copper, and those of silver, which are needles, are white and very brilliant. The solution of fluoride of silicon in alcohol being introduced into the small tube by Dr. Bird, a deposition of silicon upon the platinum was found to take place in 24 hours, which was nearly black and granular, and is described as exhibiting a tendency to a crystalline form. From an aqueous solution of the same fluoride, a deposition of gelatinous silica was observed to take place around the reduced silicon, mixed with which, or precipitated in a zone on the sides of the tube, especially if of small diameter, frequently appear minute crystalline grains of silica or quartz, of sufficient hardness to scratch glass, and appearing translucent under the microscope. With a modification of the decomposing cell described, Dr. Bird succeeded in decomposing a solution of chloride of potassium, and obtained an amalgam of potassium. The inner tube *c* was replaced by a small glass funnel, the lower opening of which was stopped with stucco, and which thus closed retained a weak solution of the alkaline chloride poured into it. Every thing external to this funnel remaining as usual, mercury, contained in a short glass tube, like a thimble, was placed in the funnel, and covered by the liquid, and instead of the platinum plate, a platinum wire, coiled into a spiral at the extremity, was plunged into the mercury, the other end of this wire being connected with the zinc plate *z* of the battery. The circuit having been thus completed, the mercury had swollen in eight or ten hours to double its former bulk, and when afterwards thrown into distilled water, evolved hydrogen, and

FIG. 91.



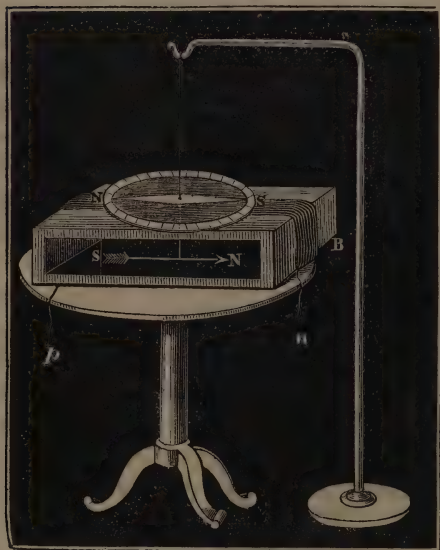
produced an alkaline solution. A solution of hydrochlorate of ammonia being substituted for that of chloride of potassium, in this experiment, the metal swells to five or six times its bulk in a few hours, and the semi-fluid amalgam of ammonium is formed. These feeble currents thus ef-

fect decompositions, in the lapse of time, which batteries of the ordinary form, and considerable magnitude, may effect very imperfectly, or fail entirely in producing.

*Volta-meter.*—The decomposing power of a battery is represented by the quantity of oxygen and hydrogen gases evolved in a cell of decomposition containing dilute sulphuric acid. The volta-meter (fig. 91) is simply a cell so charged, and of a proper form to allow of the gases evolved being collected and measured.

*Galvanometer.*—The sensibility of the magnetic needle to the influence of the conducting wire of a voltaic circle brought near it, has been applied to the construction of an instrument which will indicate the feeblest polarization or slightest current in the connecting wire. It consists of a pair of magnetic needles (fig. 92), fixed on one

FIG. 92.



axis with their attracting poles opposite each other, so as to leave them little or no directive power, and render them astatic, which is delicately suspended by a single fibre of unspun silk. The lower needle is enclosed within a circle formed by a hank of covered wire B, of which *p* and *n* are the extremities. When the terminal wires of a battery are connected with the wires, the hank of wire of the galvanometer becomes part of the connecting wire, and the needle is de-

flected. The inductions proceeding in one direction above the needle and returning in the opposite direction below the needle, conspire to produce the same deflection; and the upper needle having its poles reversed, is deflected in the same direction, by the wire below it, as the lower needle is by the wire above that needle. Every turn of the wire also repeats the influence upon the needle, so that the deflection is increased in proportion to the number of turns or coils in the hank of wire.



## CHAPTER V.

## NON-METALLIC ELEMENTS.

2 diagrams of  
Non-metallic  
Elements.

## SECTION I.—OXYGEN.

*Equivalent 8 (hydrogen = 1) or 100 as the basis of the Oxygen Scale; density 1105.6 (air = 1000); combining measure   (one volume.)*

THE following thirteen of the sixty-two elementary bodies known\*, are included in the class of non-metallic elements:—oxygen, hydrogen, nitrogen, carbon, boron, silicon or silicium, sulphur, selenium, phosphorus, chlorine, bromine, iodine, and fluorine. Of these, oxygen, from certain relations which it bears to all the others, and from its general importance, demands the earliest consideration.

The name oxygen is compounded of *οξύς*, acid, and *γεννάω*, I give rise to, and was <sup>applied</sup> given to this element by Lavoisier, with reference to its property of forming acids in uniting with other elementary bodies. Oxygen is a permanent gas, when uncombined, and forms one-fifth part of the air of the atmosphere. In a state of combination, this element is the most extensively diffused body in nature, entering as a constituent into water, into nearly all the earths and rocks of which the crust of the globe is composed, and into all organic products, with a few exceptions. It was first recognised as a distinct substance by Dr. Priestley in this country, in 1774, and about a year afterwards by Scheele in Sweden, without any knowledge of Priestley's experiments. From this discovery may be dated the origin of true chemical theory.

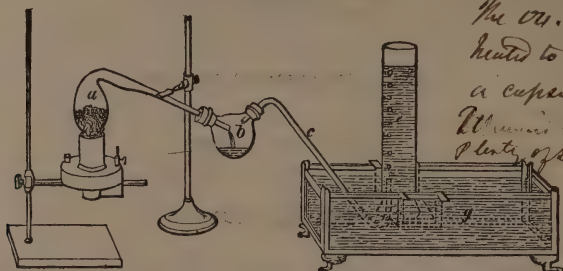
*Preparation.*—Oxygen gas is generally disengaged from some compound containing it, by the action of heat.

1. It was first procured by Priestley, by heating Red Precipitate (oxide of mercury), which is thereby resolved into fluid mercury

\* This number includes three elements—erbium, terbium, and ilmenium, of which the existence is doubtful.

and oxygen gas. To illustrate the formation of oxygen in this way, 200 grains of red precipitate may be introduced into the body of a small retort *a* of hard or difficultly fusible glass, and the retort

FIG. 93.



united in an air-tight manner with a small globular flask *b*, having two openings, both closed by perforated corks, one of which admits the beak of the retort, and the other an exit tube *c*, of glass, bent as in the figure. The extremity of the exit tube is introduced into a graduated jar capable of holding 50 or 60 cubic inches, and placed in an inverted position, full of water, upon the shelf of a pneumatic water-trough. Heat is then applied to the retort by means of an Argand spirit lamp powerful enough to raise it to a red heat, and maintain it at that temperature for a considerable time. The first effect of the heat is to expand the air in the retort, bubbles of which issue from the tube *c*, and rise to the top of the jar displacing water; but more gas follows, which is oxygen, and at the same time metallic mercury condenses in the neck of the retort and runs down into the intermediate flask *b*. When the red precipitate in the retort has entirely disappeared, the lamp may be extinguished, and the retort allowed to cool completely. The end of the exit tube *c* being now above the level of the water in the jar, which is nearly full of gas, a portion of the latter, equal in bulk to the air which first left the retort, will return to it, from the contraction of the gas within the retort. The jar will be found in the end to contain 44 cubic inches of gas, which is therefore the measure of oxygen produced in the experiment, and the flask to contain 185 grains of mercury. Now 44 cubic inches of oxygen weigh 15 grains; and a true analysis of the red precipitate has been effected, of which the result is, that 200 grains of that substance consist of—

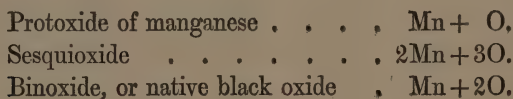
185 grains mercury.

15 „ oxygen, (44 cubic inches.)

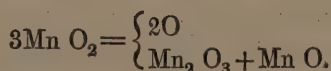
200

But oxygen gas is more generally derived from two other substances—oxide of manganese and chlorate of potash.

2. When the gas is required in large quantity, and exact purity is immaterial, the oxide of manganese is preferred from its cheapness. This is a black, heavy mineral, found in Devonshire, <sup>of Devonshire</sup> in Hesse Darmstadt, <sup>near Gießen</sup> and other localities, of which upwards of 40,000 tons are consumed annually in the manufactures of the country. It is called an oxide of manganese, because it is a compound of the metal manganese with oxygen. In explanation of what takes place when this substance is heated, it is necessary to state that manganese is capable of uniting with oxygen in several proportions, namely, one equivalent, or 27.67 parts of manganese, with 8, and with 16 parts of oxygen; and two equivalents of manganese with 24 parts of oxygen. These compounds are:—



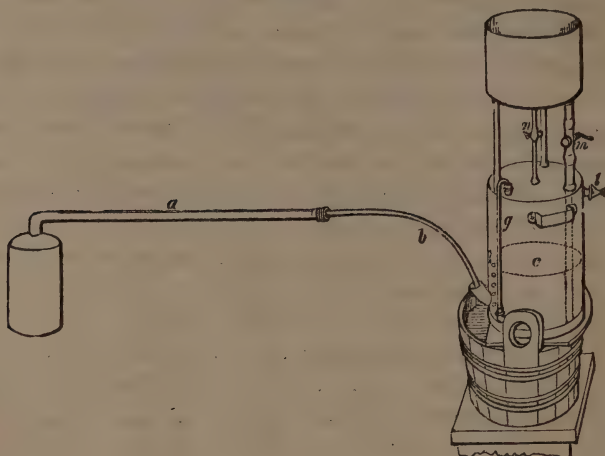
Now the binoxide, however strongly heated, never loses more than one-third of its oxygen, being converted into a compound of the first two oxides: that is, three equivalents of binoxide (131.01 parts) lose two equivalents of oxygen (16 parts), and leave a compound of one eq. of sesquioxide and one eq. of protoxide; a change which may be thus expressed:—



One of the malleable iron bottles in which mercury is imported is readily converted into a retort, in which the black oxide may be heated, by removing its screwed iron stopper, and replacing this by an iron pipe of three feet in length, one end of which has been cut to the screw of the bottle. This pipe may be bent like *a*, figure 94, if the bottle is to be heated in an open fire, or in a furnace open at the top. From 3 to 9 pounds of the oxide may be introduced as a charge, according to the quantity of gas to be prepared, each pound of good German manganese yielding about 1400 cubic inches, or 5.05 gallons of gas. Upon the first application of heat, water comes off, as steam, mixed occasionally with a gas which extinguishes flame; this is owing to the impurity of the oxide. The products may be allowed to escape, till the point of a wood-match, red without flame,

applied to the orifice, is rekindled and made to burn with brilliancy ; the gas is then sufficiently pure, and means must be taken for collecting it. A small flexible tin tube *b*, of any convenient length, is

FIG. 94.



adapted to the iron pipe, by means of a perforated cork, by which the gas is conveyed to a pneumatic trough, and collected in glass jars filled with water, as in the former experiment ; or, as this process affords considerable quantities of oxygen, the gas is more generally conducted into the inferior cylinder or drum of a copper gas holder *c*, full of water. The water does not flow out by the recurved tube which forms the lower opening, but is retained in the vessel by the pressure of the atmosphere on the surface of the water in that tube, as water is retained in a bird's drinking-glass. But when the tin tube is introduced into the gas-holder by this opening, water escapes by it, in proportion as gas is thrown into the cylinder and rises in bubbles to the top. The progress of filling the gas-holder may be observed by the glass gauge-tube *g*, which is open at both ends, and connected with the top and bottom of the cylinder, so that the water stands at the same height in the tube as in the cylinder. Convenient dimensions for the cylinder itself are 16 inches in height by 12 in diameter ; to fill which a charge of three pounds of manganese may be used. The gauge-tube is so apt to be broken, or to occasion leakage at its junctions with the cylinder, when the latter is large and unwieldy, that it is generally better to forego the advantage it offers, and dispense with this addition to the gas-holder. When applied to a small gas-holder, the ends of the tube are conveniently



adapted to the openings of the cylinder, by means of perforated corks, which are afterwards covered by a mixture of white and red lead with a drying oil.

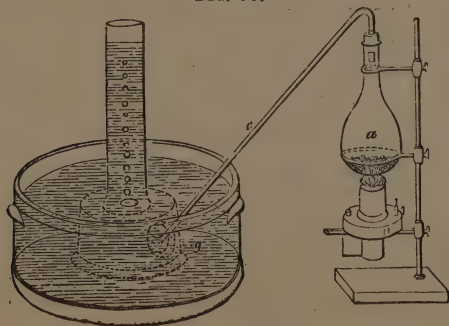
After the cylinder is filled, the lower opening by which the gas was admitted is closed by a good cork, or by a brass cap made to screw over it. The superior cylinder is an open water trough, connected with the inferior cylinder by two tubes provided with stopcocks, *m* and *n*, one of which, *m*, is continued to the bottom of that vessel, and conveys water from the superior cylinder, while the other

Fig. 95. tube, *n*, terminates at the top of the inferior cylinder, and affords a passage by which the gas can escape from it, when water is allowed to descend by the other tube. The tube and perforation of the stopcock of *m* should be considerably wider than *n*. A jar *a* is filled with gas by inverting it full of water in the superior cylinder, over the opening of *n*, as exhibited in the figure, and allowing the gas to ascend from the inferior cylinder. Gas may likewise be obtained by the stopcock *l* (fig. 94), water being allowed to enter by *m* at the same time.

Oxygen may likewise be disengaged from oxide of manganese in a flask or retort, by means of sulphuric acid diluted with an equal bulk of water, but this is not a process to be recommended. When the quantity of oxygen required is not very large, it is better to have recourse to chlorate of potash, which has also the advantage of giving a perfectly pure gas.

3. A well-cleansed Florence oil flask, the edges of the mouth of which have been heated and turned over so as to form a lip, with a bent glass tube and perforated cork fitted to it (fig. 96), forms a convenient retort in which about half an ounce of chlorate of potash may be heated by means of a gas flame or Argand spirit lamp. The salt melts, although it contains no water, and when nearly red hot emits

Fig. 96.



abundance of oxygen gas.

At one point of the decomposition, the effervescence may become so violent as to burst the flask, especially if the exit tube be narrow, unless the heat be moderated. The chlorate of potash parts with all the oxygen it possesses, which amounts to

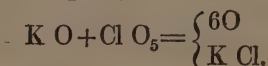
*Specimens of flask - also cork & bent tube of Kimball's method.*

39.2 per cent. of its weight, and leaves a white hard salt, the chloride of potassium.

*The Copper flask can be taken with Copper Insulator placed in Copper trough in case of fire. Have a jet upon the tube, & use the gas which continues to be evolved in powerful stream to burn antimony or charcoal; steel spring & down after being heated.*

The only inconvenience attending the preceding process is the high temperature required, which would soften a retort or flask of flint glass. It was discovered, however, by M. Mitscherlich, that chlorate of potash is decomposed at a much lower temperature when mixed with dry powders, upon which it exercises no chemical action, particularly metallic peroxides, such as the binoxide of manganese and the black oxide of copper. Nothing can answer better than the binoxide of manganese, after being made anhydrous by a short exposure to a red heat. Two parts of chlorate of potash in powder, mixed with one part of the dried oxide, forms a useful "oxygen mixture," which may be made in quantity and preserved for occasional use.

From an atomic statement of the composition of chlorate of potash it appears that one equivalent of it (122.5 parts) contains six equivalents of oxygen (48 parts), namely five eq. in the chloric acid and one eq. in the potash, the whole of which come off, leaving one equivalent of chloride of potassium (74.5 parts):—



Half an ounce of chlorate of potash should yield 270 cubic inches or nearly a gallon of pure oxygen gas.

4. Another process for oxygen gas, proposed by Mr. Balmain, consists in heating in a retort 3 parts of the bichromate of potash in powder, with 4 parts of undiluted sulphuric acid: the gas comes off in a continuous stream, and a mixture of sulphate of potash and sulphate of sesquioxide of chromium remains behind in the retort. The decomposition which takes place is explained in the following formula:—  
 $\text{KO}, \text{Cr}_2\text{O}_6$  with 4  $\text{SO}_3$ , give  $\text{KO}, \text{SO}_3$  with  $\text{Cr}_2\text{O}_3$  3 $\text{SO}_3$  and 3O.

The bichromate of potash loses one-half of the oxygen contained in the chromic acid, or about 16 per cent. of its weight; one ounce of salt yielding about 200 cubic inches of gas.

*Properties.*—Oxygen gas is colourless, and destitute of odour and taste. It is heavier than air in the ratio of 1105.6 to 1000, according to the latest careful determination, that of M. Regnault.\*

At the temperature of 60°, and with the barometer at 30 inches,

\* Annales de Chimie, &c., 1845, 3e. ser. t. xiv. p. 211. The mean of three weighings previously made by MM. Dumas and Boussingault, was 1105.7 (ibid. t. viii. p. 201). Baron Wrede found 1105.2. At a much earlier period T. de Saussure obtained Regnault's number, 1105.6. These coincidences in the results of independent observers

*g.c. To derive it from the air of the atmosphere.*

100 cubic inches of oxygen gas weigh 34.19 grains (Regnault). One cubic inch, therefore, weighs 0.3419 gr., or about  $\frac{1}{3}$  of a grain. It has never been liquefied by cold or pressure.

Oxygen is so sparingly soluble in water, that when agitated in contact with that fluid no perceptible diminution of its volume takes place. But when water is previously deprived of air by boiling, and allowed to cool in a close vessel, 100 cubic inches of it dissolve  $3\frac{1}{2}$  cubic inches of this gas.

If a lighted wax taper attached to a copper wire be blown out, and dipped into a vessel of oxygen gas, while the wick remains red hot, it instantly rekindles with a slight explosion, and burns with great brilliancy. If soon withdrawn and blown out, it may be revived again in the same manner, and the experiment be repeated several times in the same gas. Lighted tinder burns with flame in oxygen, and red-hot charcoal with brilliant scintillations. Burning sulphur introduced into this gas in a little hemispherical cup of iron-plate with a wire attached to it, burns with an azure blue flame of considerable intensity. Phosphorus introduced into oxygen in the same manner, burns with a dazzling light of the greatest splendour, particularly after the phosphorus boils and rises through the gas in vapour. Indeed, all bodies which burn in air, burn with increased vivacity in oxygen gas. Even iron wire may be burned in this gas. For this purpose thin harpsichord wire should be coiled about a cylindrical rod into a spiral form. The rod being withdrawn, a piece of thread must be twisted about one end of the wire, and dipped into melted sulphur; the other end of the wire is to be fixed into a cork, so that the spiral may hang vertically. The sulphured end is then to be lighted, and the wire suspended in a jar of oxygen, open at the bottom, such as that represented in fig. 95, page 295, supported upon an earthenware plate. The wire is kindled by the sulphur, and burns with an intense white light, throwing out a number of sparks, or occasionally allowing a globule of fused oxide to fall; while the wire itself continues to fuse and burn till it is entirely consumed, or the oxygen is exhausted. The experiment forms one of the most

appear to prove that a close approximation has been made to the true density of this gas: an important datum. The earlier determination of MM. Dulong and Berzelius was 1102.6 (ibid. 1820, 2e. ser. t. xv. p. 386). According to M. Regnault the weight of 1000 cubic centimeters (1 liter) of oxygen gas, at 32° F., barometer 29.92 inches (760 millimeters), is 1.4298 gramme. Hence, 1000 c. c. being equal to 61.028 English c. inches, and 1 gramme to 15.4440 English grains, 100 cubic inches of oxygen, at the specified temperature and pressure, weigh 36.1890 grains. Calculating with Regnault's coefficient for the expansion of air (page 12), 1 volume of oxygen will become 1.05701 volume, at 60°, and 100 cubic inches of oxygen will weigh 34.1898 grains at that temperature.

*Green way*

*hard steel wire  
over clear  
water, first day  
I returned to  
soft wire over  
red litmus till  
next day at  
huge 302.*



beautiful and brilliant in chemistry. The globules of fused oxide are of so elevated a temperature, that they remain red-hot for some time under the surface of water, and fuse deeply into the substance of the stoneware plate upon which they fall.

*Monday  
Nov. 5, 1849.* Oxygen gas is respirable, and indeed is constantly taken into the lungs from the atmosphere in ordinary respiration. When a portion of dark blood drawn from a vein is agitated with this gas, the colour becomes of a fine vermilion red. The same change occurs in the blood of living animals, during respiration, from the absorption of oxygen gas, which is required to maintain the animal heat. A small animal, also, such as a mouse or bird, lives four or five times longer in a vessel of oxygen than it will in an equal bulk of air. But the continued respiration of this gas in a state of purity is injurious to animal life. A rabbit is found to breathe it without inconvenience for some time, but after an interval of an hour or more the circulation and respiration are much quickened, and a state of great excitement of the general system supervenes; this is by and by followed by debility, and death occurs in from six to ten hours. The blood is found to be highly florid in the veins as well as the arteries, and, according to Broughton, the heart continues to act strongly after the breathing has ceased.

*Roman* Oxygen may be made to unite with all the other elements except fluorine, and forms *oxides*, while the process of uniting with oxygen is termed *oxidation*. With the same element oxygen often unites in several proportions, forming a series of oxides, which are then distinguished from each other by the different prefixes enumerated under *Chemical Nomenclature* (page 113). Many of its compounds are *acids*, particularly those which contain more than one equivalent of oxygen to one of the other element, and compounds of this nature are those which it most readily forms with the non-metallic elements: such as carbonic acid with carbon, sulphurous acid with sulphur, phosphoric acid with phosphorus. But oxygen unites in preference with single equivalents of a large proportion of the metallic class of elements, and forms bodies which are alkaline or have the character of *bases*: such as potash, lime, magnesia, protoxide of iron, &c. A certain number of its compounds are neither acid nor alkaline, and are therefore called *neutral* bodies: such as the oxide of hydrogen or water, carbonic oxide, and nitrous oxide. The greater number of these neutral oxides are also protoxides.

It has already been stated that in a classification of the elements oxygen does not stand alone, but forms one of a small natural family along with sulphur, selenium, and tellurium. These elements also



form acid, basic, and neutral classes of compounds, with the same bodies as oxygen does, of which the sulphur compounds are well known, and always exhibit a well-marked analogy to the corresponding oxides. Oxygen-acids unite with oxygen-bases, and form neutral *salts*: so do sulphur-acids with sulphur-bases, selenium-acids with selenium-bases, and tellurium-acids with tellurium-bases.

The combinations of oxygen, like those of all other bodies, are attended with the evolution of heat. This result, which is often overlooked in other combinations, in which the proportions of the bodies uniting and the properties of their compound receive most attention, assumes an unusual degree of importance in the combinations of oxygen. The economical applications of the light and heat evolved in these combinations are of the highest consequence and value, and oxidation alone, of all chemical actions, is practised, not for the value of the products it affords, and indeed without reference to them, but for the sake of the incidental phenomena attending it. Of the chemical combinations, too, which we habitually witness, those of oxygen are infinitely the most frequent, which arises from its constant presence and interference as a constituent of the atmosphere. Hence, when a body combines with oxygen, it is said to be *burned*; and instead of undergoing oxidation, it is said to suffer *combustion*; and a body which can combine with oxygen and emit heat is termed a *combustible*. Oxygen, in which the body burns, is then said to support combustion, and called a *supporter* of combustion.

The heat evolved in combustion is definite, and can be measured. With this view it is employed to melt ice, to raise the temperature of water from  $32^{\circ}$  to  $212^{\circ}$ , or to convert water into steam, and its quantity estimated by the extent to which it produces these effects. The heat from the oxidation of a combustible body is thus found to be as constant as any other of its properties. Despretz obtained, by such experiments, the results contained in the following table:—

## HEAT FROM COMBUSTION.

1 pound of pure charcoal . . . . .	heats from $32^{\circ}$ to $212^{\circ}$ , 78 pounds of water.
— charcoal from wood . . . . .	75 —
— baked wood . . . . .	36 —
— wood containing 20 per cent. of water . . . . .	27 —
— bituminous coal . . . . .	60 —
— turf . . . . .	25 to 30 —
— alcohol . . . . .	67.5 —
— olive oil, wax, &c. . . . .	90 to 95 —
— ether . . . . .	80 —
— hydrogen . . . . .	236.4 —

The quantity of heat evolved appears to be connected with the proportion of oxygen consumed, for the greater the weight of oxygen with which a pound of any combustible unites, the more heat is produced. The following results indicate that the heat depends exclusively upon the oxygen consumed, four different combustibles in consuming a pound of oxygen affording nearly the same quantity of heat :—

## HEAT OF COMBUSTION.

1 pound of oxygen with hydrogen heats from  $32^{\circ}$  to  $212^{\circ}$ ,  $29\frac{1}{2}$  pounds of water.

—	with charcoal	—	29	—
—	with alcohol	—	28	—
—	with ether	—	$28\frac{1}{2}$	—

The quantity of combustible consumed in these experiments varied considerably, but the oxygen being the same, the heat evolved was nearly the same also. ~~But~~ When the same quantity of oxygen <sup>however</sup> converted phosphorus into phosphoric acid, exactly twice as much heat was evolved, according to Despretz, as in the former experiments. The superior vivacity of the combustion of these and other bodies in pure oxygen, compared with air, depends entirely upon the rapidity of the process, and the larger quantity of combustible oxidated in a given time. A candle burns with more light and heat in oxygen than in air, but it consumes proportionally faster.

Oxidation is often a ~~very~~ slow process, and imperceptible in its progress—as in the rusting of iron and tarnishing of lead exposed to the atmosphere. The heat being then evolved in a gradual manner is instantly dissipated, and never accumulates. But when the oxide formed is the same, the nature of the change effected is in no way altered by its slowness. Iron oxidates rapidly when introduced in a state of ignition into oxygen gas, and lead, in the form of the lead pyrophorus, which contains that metal in a high state of division, takes fire spontaneously and burns in the air; circumstances then favouring the rapid progress of oxidation.

Oxidation may also go on with a degree of rapidity sufficient to occasion a sensible evolution of heat, but without flame and open combustion. The absorption of oxygen by spirituous liquors in becoming acetic acid, and by many other organic substances, is always attended with the production of heat. The smouldering combustion of iron pyrites and some other metallic ores in the atmosphere, is a phenomenon of the same nature. Most bodies which burn with flame also admit of being oxidated at a temperature short of redness, and exhibit the phenomenon of *low combustion*. Thus, *tallow* <sup>Basin</sup> thrown upon an iron plate not visibly red hot, melts and undergoes

oxidation, diffusing a pale lambent flame only visible in the dark (Dr. C. J. B. Williams). If the ~~tallow~~ <sup>metal</sup> be heated in a little cup with a wire attached, till it boils and catches fire, and the flame then be blown out, the hot tallow will still continue in a state of low combustion, of which the flame may not be visible, but which is sufficient to cause the renewal of the high combustion, if the cup is immediately introduced into a jar of oxygen gas. A candle newly blown out is sometimes rekindled in oxygen, although no point of the wick remains visibly red, owing to the continuance of this low combustion. When a coil of thin platinum wire, or a piece of platinum foil, is first heated to redness, and then held over a vessel containing ether or hot alcohol, the vapours of these substances, mixed with the air, oxidate upon the hot metallic surface, and may sustain the ~~vessel~~ <sup>metal</sup> at a red heat for a long time, without the occurrence of combustion with flame. The product, however, of the low combustion of these bodies is peculiar, as is obvious from its pungent odour.

*Combustion in air.*—The affinity for oxygen of all ordinary combustibles is greatly promoted by heating them, and is indeed rarely developed at all except at a high temperature. Hence, to determine the commencement of combustion, it is commonly necessary that the combustible be heated to a certain point. But the degree of heat necessary to inflame the combustible is in general greatly inferior to what is evolved during the progress of the combustion, so that a combustible, once inflamed, maintains itself sufficiently hot to continue burning till it is entirely consumed. Here the difference may be observed between combustion and simple ignition. A brick heated till it be red-hot in a furnace, and taken out, exhibits ignition, but has no means within itself of sustaining a high temperature, and soon loses the heat which it had acquired in the fire, and on cooling is found unchanged.

The oxidable constituents of wood, coal, oils, tallow, wax, and all the ordinary combustibles, are the same, namely, carbon and hydrogen, which in combining with oxygen, at a high temperature, always produce carbonic acid and water; volatile bodies, which disappear, forming part of the aerial column that rises from the burning body. The constant removal of the product of oxidation, thus effected by its volatility, greatly favours the progress of combustion in such bodies, by permitting the free access of air to the unconsumed combustible. The interference of air in combustion is obvious from the facility with which a fire is checked or extinguished when the supply of air is lessened or withheld, and, on the contrary,



revived and animated when the supply of air is increased by blowing up the fire. For the oxygen of the air being consumed in combining with the combustible, a constant renewal of it is necessary. Hence, if a lighted taper, floated by a cork upon water, be covered with a bell jar having an opening at top, such as that in which the iron-wire was burned, the taper will burn for a short time without change, then more and more feebly, in proportion as the oxygen is exhausted, and at last will expire. The air remaining in the jar is no longer suitable to support combustion, and a second lighted taper introduced into it by the opening at top is immediately extinguished.

In combustion, no loss whatever of ponderable matter occurs; nothing is annihilated. The matter formed may always be collected without difficulty, and is found to have exactly the weight of the oxygen and combustible together which have disappeared. The most simple illustrations of this fact are obtained in the combustion of those bodies which afford a solid product. Thus when two grains of phosphorus are kindled in a measured volume of oxygen gas, they are found converted after combustion into a quantity of white powder (phosphoric acid), which weighs  $4\frac{1}{2}$  grains, or the phosphorus acquires  $2\frac{1}{2}$  grains; at the same time  $7\frac{1}{2}$  cubic inches of oxygen disappear, which weigh exactly  $2\frac{1}{2}$  grains. In the same way, when iron wire is burned in oxygen, the weight of solid oxide produced is found to be equal to that of the wire originally employed added to that of the oxygen gas which has disappeared. But the oxidation of mercury affords a more complete illustration of what occurs in combustion. Exposed to a moderate degree of heat for a considerable time in a vessel filled with oxygen, that metal is converted into red scales of oxide, possessing the additional weight of a certain volume of oxygen which has disappeared. But if the oxide of mercury so produced be then put into a small retort, and reconverted by a red heat into oxygen and fluid mercury, the quantity of oxygen emitted is found to be the same as had combined with the mercury in the first part of the operation; thus proving that oxygen is really present in the oxidized body.

The evolution of heat, which is the most striking phenomenon of combustion, still remains to be accounted for. It has been referred to the loss of latent heat by the combustible and oxygen, when, from the condition of gas or liquid, one or both become solid after combustion; to a reduction of capacity for heat, the specific heat of the product being supposed to be less than that of the bodies burned; and to a discharge of the electricities belonging to the different bodies,

*Iron wire  
in oxygen  
over and above*



occurring in the act of combination. But the first two hypotheses are manifestly insufficient, and the last is purely speculative. The evolution of heat during intense chemical combination, such as oxidation, may be received at present as an ultimate fact; but if we choose to go beyond it, we must suppose that the heat exists in a combined and latent state in either the oxygen or combustible, or in both; that each of these bodies is a compound of its material basis with heat, the whole or a definite quantity of which they throw off on combining with each other. Heat, like other material substances, is here supposed not to evince its peculiar properties while in a state of combination with other matter, but only when isolated and free. This view gives a literal character to the expressions—liberation, disengagement, and evolution of heat during combustion. The phenomenon, it is to be remembered, is not confined to oxidation, but occurs in an equal degree in combinations without oxygen, and indeed to a greater or less extent in all chemical combinations whatever.

FIG. 97.

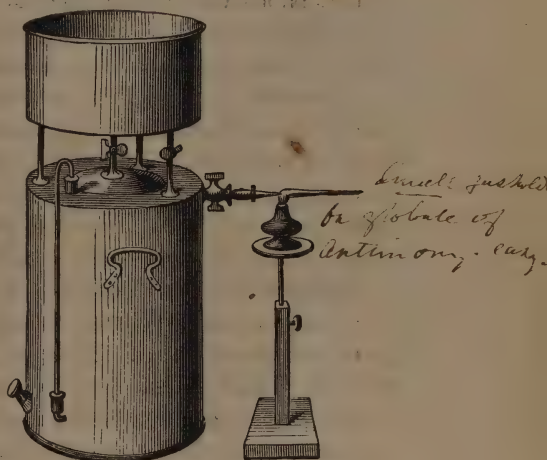
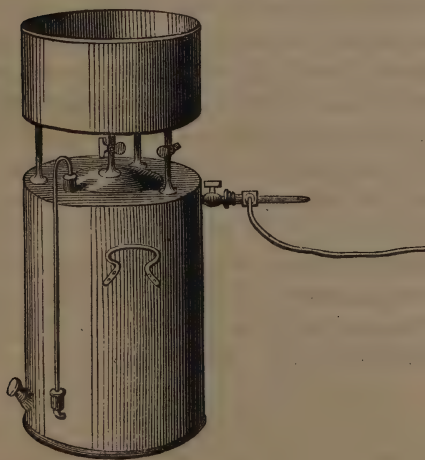


FIG. 98.



Pure oxygen has not as yet found any considerable application in the arts. But by the chemist it is applied to support combustion with the view of producing intense heat. A jet of this gas from a gas-holder (fig. 97), thrown upon the flame of a spirit lamp, produces a blow-pipe flame of great intensity, adequate to fuse platinum. Or, if coal-gas be conducted to the oxygen jet (fig. 98), and

the gases kindled as they issue together, aflame is produced of equally high temperature. Where a large quantity of oxygen is required, as in this application of it, the gas may be obtained by heating oxide of manganese in a cylinder of cast iron supported over a furnace, like the retort for coal gas. The calcined oxide does not regain its oxygen when afterwards exposed to the air, as was once supposed, but would still be of some value in the preparation of chlorine.

*Ozone.*—When electric sparks are taken through perfectly dry oxygen, a small portion of the gas acquires new properties, according to A. de la Rive, and is supposed by Berzelius to pass into an allotropic condition, in which it is named ozone from the peculiar odour it possesses, and which is somewhat metallic in character. The oxygen evolved from the decomposition of water in the voltameter (page 289) has the same odour. But the most ready mode of producing it is to place a few sticks of phosphorus in a quart bottle containing a little water at the bottom of it. While the sticks of phosphorus undergo the low combustion and are luminous, producing fumes of phosphorous acid and absorbing much oxygen, they give rise to the appearance of ozone in the air of the bottle in a manner not at present understood.

This substance has never been obtained in a separate state, but air impregnated with it acts very much as if a trace of chlorine gas were present, which ozone appears to resemble. In ozonized air, paper impregnated with a solution of iodide of potassium immediately becomes brown from the liberation of iodine; also paper containing a solution of sulphate of manganese soon becomes brown or black, from the formation of binoxide of manganese. The same air made to stream through a solution of the yellow ferrocyanide of potassium converts it into the red ferricyanide. Ozone appears to be a gas not sensibly dissolved by water. It is destroyed by a heat of  $140^{\circ}$ , by contact with olefiant gas, and such other hydrocarbons as combine with chlorine, by phosphorus, or reduced silver. In the latter case nothing appears except oxide of silver. It passes, I find, through dry and porous stoneware, and is therefore not likely to be merely an electrical grouping of gaseous molecules. Professor Schönbein, who named this substance, and has made it the object of many investigations, considers it to be a volatile peroxide of hydrogen.

*Ozone.* Have not phosphorus & common "Sulphuric Acid", allotropic? The mere opening of the bottles & admitting fresh air appears to destroy the ozone. Certainly also so, with paper introduced at some time.

*OZONE* - in K I thickened with starch. Sulphate of manganese made as neutral as possible? The oxygen has a susceptibility common to it like that given to the silver foil in the solution of potassium.

## SECTION II.

## HYDROGEN.

*Equivalent 1, as the basis of the Hydrogen Scale, or 12.5 (oxygen = 100); symbol H; density 69.26 (air 1000); combining measure      (two volumes.)*

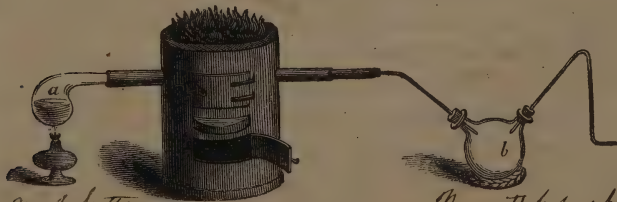
Hydrogen gas, which was long confounded with other inflammable airs, was first correctly described by Cavendish, in 1766. It does not exist uncombined in nature; at least the atmosphere does not contain any appreciable proportion of hydrogen. But it is one of the elements of water, and enters into nearly every organic substance. Its name is derived from  $\text{ἰδωρ}$ , water, and  $\gamma\epsilon\nu\nu\alpha\omega$ , I give rise to, and refers to its forming water when oxidated.

*Preparation.*—This element, although resembling oxygen in being a gas, appears to be more analogous to a metal in its relations to other elements. By heating oxide of mercury, it is resolved into oxygen and mercury; and several other metallic oxides, such as those of silver and gold, are susceptible of a similar decomposition. But some others are deprived of only a portion of their oxygen by the most intense heat, such as bin<sup>ous</sup>oxide of manganese; and many, such as the protoxide of lead, are not decomposed at all by simple calcination. By igniting the latter oxide, however, mixed with charcoal, its oxygen goes off in combination with carbon, as carbonic oxide, and the lead is left. The oxide of hydrogen or water is similarly affected. Potassium and sodium brought into contact with it, at the temperature of the air, combine with its oxygen, and are converted into the oxides potash and soda; and hydrogen is consequently liberated.

*See over page.*

Iron and many other metals decompose water, and become oxides, at a red heat. Hence, hydrogen gas is sometimes procured by transmitting steam through an iron tube filled with iron turnings, placed across a furnace and heated red-hot (fig. 96).

FIG. 96.



*Gas much better than sp. lamp.*

*Throw H before hand into it.*

*Open furnace collect two jars & then this cannot be dangerous.*

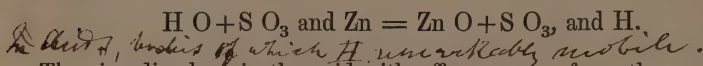


The vapour is obtained by boiling water in the small retort *a*, and the gas produced by its decomposition collected in the usual manner at the pneumatic trough. But it is necessary to have a flask *b* between the iron tube and the trough, to prevent an accident from the water of the trough finding access to the red hot tube, in the event of condensation of the vapour in *a*.

Some other compounds of hydrogen are decomposed more easily than water, by iron and zinc. The chloride of hydrogen or hydrochloric acid is decomposed by these metals, and evolves hydrogen at the ordinary temperature of the air. But this gas is more generally obtained by putting pieces of zinc or iron into oil of vitriol or the concentrated sulphuric acid, diluted with six or eight times its bulk of water. The hydrogen is then derived from the decomposition of the proportion of water intimately united with the acid, as illustrated in the following diagram, zinc being used, and the quantities expressed:—

Before decomposition.			After decomposition.	
49	oil of vitriol, or sulphate of water . . .	{ Hydrogen . . . 1 Oxygen . . . 8 Sulphuric acid 40	1	Hydrogen.
32.52	zinc . . . .	Zinc . . . . 32.52	80.52	Sulphate of oxide of zinc.
81.52		81.52	81.52	

Or by symbols:—



The zinc dissolves in the acid with effervescence, from the escape of hydrogen gas. It will be observed that the products after decomposition, mentioned in the last column, hydrogen and sulphate of oxide of zinc, are similar to those before decomposition, in the first column, zinc and sulphate of water; and that the change occurring is simply the *substitution* of zinc for hydrogen in the sulphate of water. The large quantity of water used with the acid is useful to dissolve the sulphate of zinc formed.

Zinc is generally preferred to iron, in the preparation of hydrogen, and is previously granulated, by being fused in a stone-ware crucible, and poured into water; if sheet zinc be used, which is better, it is cut into small pieces. The common glass retort may be used in the experiment, or a gas-bottle, such as the half-pound phial (fig. 97), with a cork having two perforations fitted with glass tubes, one of which descends to the bottom of the bottle, and is terminated externally by a funnel



Fig. 97.



*A Gas the Soldering  
Lead in Apparatus  
Dr. Hoffman - In Pet.  
Charge it time  
2 lbs acid in  
beaker; mix in jar.*

for introducing the acid, whilst the other is the exit tube, by which the hydrogen escapes. With an ounce or two of zinc in it, the bottle is two-thirds filled with water, and the undiluted acid added from time to time by the funnel, so as to sustain a continued effervescence. No gas escapes by the funnel tube, as its extremity within the bottle is always covered by the fluid. To produce large quantities, a half-gallon stone-ware jar may be mounted as a gas bottle, with a flexible metallic

pipe fitted to the cork as the exit tube. This gas may be collected, like oxygen, either in jars over the pneumatic trough, or in the gas-holder. The first jar or two filled will contain the air of the gas-bottle, and therefore must not be considered as pure hydrogen. One ounce of zinc is found to cause the evolution of 615 cubic inches of hydrogen gas.

**Properties.**—Hydrogen gas thus prepared is not absolutely pure, but contains traces of sulphuretted hydrogen and carbonic acid, which may be removed by agitating the gas with lime-water or caustic alkali. It has also a particular odour, which is not essential to hydrogen, as the gas evolved from the amalgam of sodium, acted on by pure water without acid, is perfectly inodorous. An oily compound of carbon and hydrogen, which appears to be the cause of this odour, may be separated in a sensible quantity from the gas prepared by iron, by transmitting it through alcohol. Of the pure gas, water does not dissolve more than  $1\frac{1}{2}$  per cent. of its bulk. Hydrogen has never been liquefied by cold or pressure.

Hydrogen is the lightest substance in nature, being sixteen times lighter than oxygen, and 14.4 times lighter than air; 100 cubic inches of it weigh only 2.14 grains. Soap-bubbles blown with this gas ascend in the atmosphere; and it is used, as is well known, to inflate balloons, which begin to rise when the weight of the stuff of which they are made and the hydrogen together, are less than the weight of an equal bulk of air. A light bag is prepared for making this experiment in the chamber, by distending the lining membrane of the crop of the turkey, which may weigh 35 or 36 grains, and when filled with hydrogen, about 5 grains more, or 41 grains; the same bulk of air, however, would weigh 50 or 51 grains; so that the little

*it is easy to find that zinc which gives no  $H_2$ , & is thus  
free from As.*

balloon when filled with hydrogen has a buoyant power of 9 or 10 grains. Larger bags are prepared for the same purpose, of gold-beaters' skin. Sounds produced in this gas were found by Leslie to be extremely feeble; much more feeble, indeed, than its rarity compared with air could account for. <sup>pure</sup> Hydrogen may be taken into the lungs without inconvenience, when mixed with a large quantity of air, being in no way deleterious; but it does not, like oxygen, support respiration, and therefore an animal placed in pure hydrogen soon dies of suffocation. A lighted taper is extinguished in the same gas.

Hydrogen is eminently combustible, and burns when kindled in the air with a yellow flame of little intensity, which moistens a dry glass jar held over it; the gas combining with the oxygen of the air in burning, and producing water. If before being kindled the gas is first mixed with enough of air to burn it completely, or with between two and three times its volume, and then kindled, the combustion of the whole hydrogen is instantaneous and attended with explosion. With pure oxygen, instead of air, the explosion is much more violent, particularly when the gases are mixed in the proportions of two volumes of hydrogen to one of oxygen, which are the proper quantities for combination. The combustion is not thus propagated through a mixture of these gases, when either of them is in great

FIG. 98.



also brass  
& zinc pipes

excess. The sound in such detonations is occasioned by the concussion which the atmosphere receives from the sudden dilatation of gaseous matter, in this case of steam, which is prodigiously expanded from the heat evolved in its formation.

A musical note may be produced by means of these detonations, when they are made to succeed each other very rapidly. If hydrogen be generated in a gas bottle (fig. 98), and kindled as it escapes from an upright glass jet having a small aperture, the gas will be found to burn tranquilly; but on holding an open glass tube of about two feet in length over the jet, like a chimney, the flame will be elongated and become flickering. A succession of little detonations is produced, from the gas being carried up and mixing with the air of the tube, which follow each other so quickly as to produce a continuous sound or musical note.

Several circumstances affect the combination of hydrogen with oxygen, which are important. These gases may be mixed together in

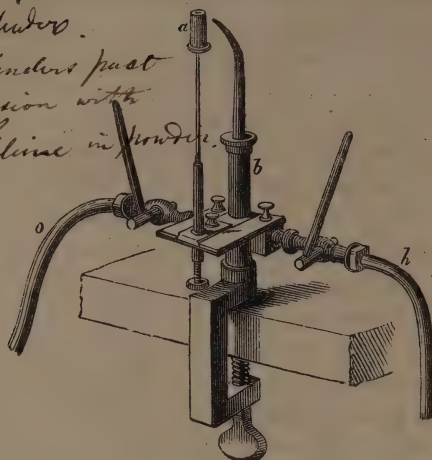
a glass vessel, and preserved for any length of time without combining. But combination is instantly determined by flame, by passing the electric spark through the mixture, or even by introducing into it a glass rod, not more than just visibly red-hot. Hydrogen, indeed, is one of the more easily inflammable gases. If the mixed gases be heated in a vessel containing a quantity of pulverized glass, or any sharp powder, they begin to unite in contact with the foreign body in a gradual manner without explosion, at a temperature not exceeding  $660^{\circ}$ . The presence of metals disposes them to unite at a still lower temperature; and of the metals, those which have no disposition of themselves to oxidate, such as gold and platinum, occasion this slow combustion at the lowest temperature. In 1824, Döbereiner made the remarkable discovery that newly prepared spongy platinum has an action upon hydrogen mixed with oxygen, independently of its temperature, and quickly becomes red-hot when a jet of hydrogen is thrown upon it in air, combination of the gases being effected by their contact with the metal. In consequence of this ignition of the platinum the hydrogen itself is soon inflamed, as it issues from the jet. An instrument depending upon this action of platinum has been constructed for producing an instantaneous light. Afterwards, Mr. Faraday observed, that the divided state of the platinum, although favourable, is not essential to this action; and that a plate of that metal, if its surface be scrupulously clean, will cause a combination of the gases, accompanied with the same phenomena as the spongy platinum. This action of platinum is manifested at temperatures considerably below the freezing point of water, and in an explosive mixture largely diluted with air or hydrogen. Spongy platinum, made into pellets with a little pipe-clay, and dried, when introduced into mixtures of oxygen and hydrogen will be found to cause a gradual and silent combination of the gases, in whatever proportions they are mingled, which will not cease till one of them is completely exhausted. The theory of this effect of platinum is very obscure. It belongs to a class of actions depending upon surface, not confined to that metal, and by which other combustible vaporous bodies are affected besides hydrogen.

The flame of hydrogen, although so slightly luminous, is intensely hot; few combinations producing so high a temperature as the combustion of hydrogen. In the oxi-hydrogen blow-pipe, oxygen and hydrogen gases are brought by tubes *o* and *h* (fig. 99, p. 310), from different gas-holders, and allowed to mix immediately before they escape by the same orifice, at which they are inflamed. This is most

*Pluto o  
Faraday  
to show*

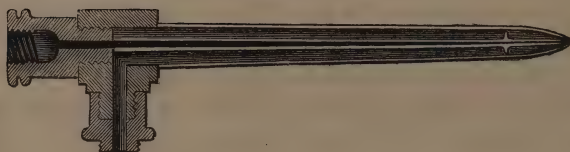


Fig. 99.



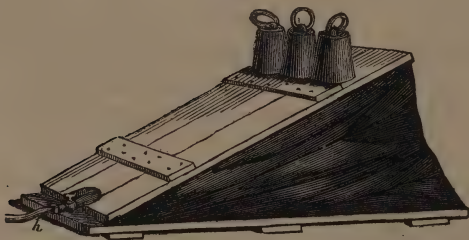
safely effected by fixing a jet for the oxygen within the jet of hydrogen (fig. 100), so that the oxygen is introduced into the middle of the flame of hydrogen—a construction first proposed by Mr. Maugham, and adapted to the use of coal-gas instead of hydrogen by Mr. Daniell.\* Each of the gases may be more conveniently contained in a separate air-tight bag of

Fig. 100.



Macintosh cloth capable of holding from 4 to 6 cubic feet of gas, and provided with press-boards. These require to be loaded with two or three 56lbs., when in use, to send out the gas with suffi-

Fig. 101.



cient pressure. At this flame the most refractory substances, such as pipe-clay, silica and platinum, are fused with facility, and the latter even dissipated in the state of vapour. The flame itself, owing to

the absence of solid matter, is scarcely luminous, but any of the less fusible earths, upon which it is thrown,—a mass of quick-lime, for instance (*a*, fig. 99),—is heated most intensely, and diffuses a light, which, for whiteness and brilliancy, may be compared to

\* Phil. Mag. 3rd Series, Vol. ii. p. 57



that of the sun. With the requisite supply of the gases, this light may be sustained for hours, care being taken to move the mass of lime slowly before the flame, so that the same surface may not be long acted upon; for the high irradiating power of the lime is soon impaired, it is supposed from a slight agglutination of its particles occasioned by the heat. This light, placed in the focus of a parabolic reflector, was found to be visible, in the direction in which it was thrown, at a distance of 69 miles, in one experiment made by Mr. Drummond, when using it as a signal light. The heating effects are even more intense when the gases are forced into a common receptacle, and allowed to escape from under pressure, but there is the greatest risk of the flame passing back through the exit tube and exploding the mixed gases; an accident which would expose the operator to the greatest danger. Mr. Hemming's apparatus, however, may be used without the least apprehension. A common bladder is used to hold the mixture, and the gas before reaching the jet, at which it is burned, is made to pass through his safety tube. This consists of a brass cylinder about six inches long and  $\frac{3}{4}$ ths of an inch wide, filled with fine brass wire of the same length, which is tightly wedged by forcibly inserting a pointed rod of metal into the centre of the bundle. The conducting power of the metallic channels through which the gas has then to pass is so great as completely to intercept the passage of flame. A similar safety tube of smaller size is interposed at *b*, in fig. 99, of the first arrangement.

Hydrogen is capable of forming two compounds with oxygen, namely water, which is the protoxide, and the binoxide of hydrogen.

The most important of the present applications of hydrogen gas is in the oxi-hydrogen blow-pipe. It has been superseded, as a material for inflating balloons, by coal gas, the balloon being proportionally enlarged to compensate for the less buoyancy of the latter gas.

#### PROTOXIDE OF HYDROGEN.—WATER.

*Equivalent 9, or 112.5 on the oxygen scale; formula  $H + O$ , or  $H O$ ; density 1; as steam 622 (air 1000); combining measure of steam*

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*.*

Mr. Cavendish first demonstrated, in 1781, that the product of the combustion of hydrogen and oxygen is water. He burned

*Int. heat capacity.*

known quantities of these gases in a dry glass vessel, and found that water was formed in quantity exactly equal to the weights of the gases which disappeared. It was afterwards established by Humboldt and Gay-Lussac, that the gases unite rigorously in the proportion of two volumes of hydrogen to one volume of oxygen, and that the water produced by their union occupies, while it remains in the state of vapour, exactly two volumes (page 143). The proportion of the constituents of water by weight was determined with great care by Berzelius and Dulong. Their method was to transmit dry hydrogen gas over a known weight of the black oxide of copper, contained in a glass tube, and heated to redness by a lamp. The gas was afterwards conveyed through another weighed tube containing the hygro-metric salt, chloride of calcium. The hydrogen gas in passing over the oxide of copper, combines with its oxygen and forms water, which is carried forward by the excess of hydrogen gas, and absorbed in the chloride of calcium tube. The weight of this water being ascertained, the proportion of oxygen it contains is determined by ascertaining the loss which the oxide of copper has sustained: the difference is the hydrogen.

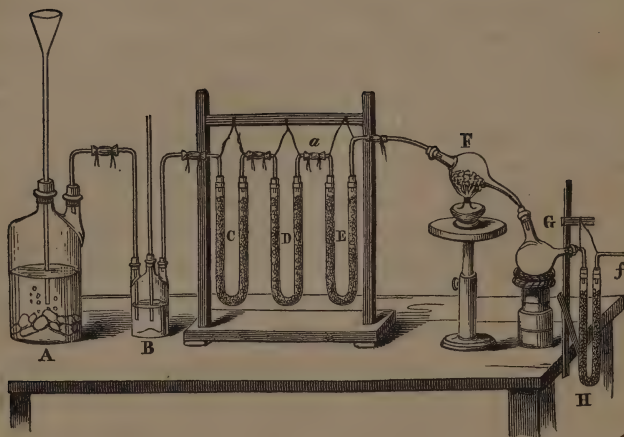
The apparatus for such an experiment is illustrated in the following diagram (fig. 102). The oxide of copper to be reduced is contained in F, a small flask of hard glass, having two openings, and heated by a spirit lamp. This flask communicates with another, G, intended to receive the greater part of the water produced in the experiment, which is followed by a bent tube H, containing fragments of pumice soaked in oil of vitriol, intended to receive the last portions. The hydrogen gas for this purpose must be very pure, and thoroughly dry. It is evolved slowly from a gas-bottle A, and passes through a second bottle B, and the bent tube C, both containing a concentrated solution of caustic potash, and afterwards the bent tube D, containing a solution of chloride of mercury in pumice: and lastly through the bent tube ~~F~~, containing oil of vitriol in pumice, proceeding thence entirely purified into F, and the excess of hydrogen gas escaping by *f*. Numerous most careful experiments, lately executed in this manner by M. Dumas, prove that water consists exactly by weight of—

Oxygen	.	.	.	88.91	.	8
Hydrogen	.	.	.	11.09	.	1
<hr/>						
100.00						9

*Diagram of Expt.*

The oxygen and hydrogen are therefore combined exactly in the

FIG 102.



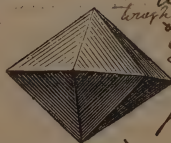
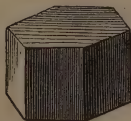
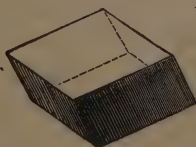
proportion of 8 to 1, as appears by the proportions of the last column. This experiment serves not only to determine rigorously the composition of water, but it offers also the best method of ascertaining the composition of such metallic oxides as are de-oxidized by hydrogen.

Colour of water & ice  
blue. Benar

920 Leones  
9184 Pliny  
I Loue

*Properties.*—When cooled down to  $32^{\circ}$ , water freezes, if in a state of agitation, but may retain the liquid condition at a lower temperature, if at rest (page 42); the ice, however, into which it is converted cannot be heated above  $32^{\circ}$  without melting. Ice is lighter than water, its specific gravity being 0.916; and one of the forms (fig. 103) of its crystal is a rhomboid, very nearly resembling Iceland spar.

FIG. 103.





through which the steam has passed. When mixed with air, the vapour of water has a tendency to condense, it is said in vesicles, which inclose air; forming in this condition the masses of clouds, which remain suspended in the atmosphere from the lightness of the vesicles, the substance of mists and fogs, and "vapour" generally, in its popular meaning. The vesicles may be observed by a lens of an inch focal length, over the dark surface of hot tea or coffee, mixed with an occasional solid drop which contrasts with them. According to the experiments of Saussure, made upon the mists of high mountains, these vesicles generally vary in size from the 1-4500th to the 1-2780th of an inch, but are occasionally observed as large as a pea. They are generally condensed by their collision into solid drops, and fall as rain; but their precipitation in that form is much retarded in some conditions of the atmosphere. It is proper to add, however, that Prof. J. Forbes and several other eminent meteorologists disbelieve entirely the existence of vesicular vapour.

*Expt. with hot water in glass breaker. Remove from water while still not hot. Gas flame held behind.*

It was lately discovered by Mr. Grove that the vapour of water is decomposed to a small but sensible extent by an exceedingly high temperature, and resolved into its constituent gases. If a small ball of platinum, of the size of a large pea, with a wire attached to it, be heated in the flame of the oxi-hydrogen blow-pipe to bright whiteness, and till it begins to show symptoms of fusion, and then plunged into hot water, minute bubbles of gas rise with the steam, which consist of a mixture of oxygen and hydrogen. Only a small portion of the steam, not amounting to even one-thousandth part of the whole produced (it is supposed), suffers decomposition. The occurrence of a decomposition in such circumstances, which is unquestionable, appears singular, seeing that oxygen and hydrogen certainly combine at the same, or even a higher, temperature in the flame of the blow-pipe, which is employed to heat the platinum ball. The combustion in the blow-pipe may, indeed, be incomplete, but this is unlikely, for I find that when the mixed gases are exploded in a glass tube, the combustion is so complete that certainly not one part in four thousand, if any portion whatever, escapes combustion. It is a question whether the decomposition of the steam by ignited platinum is not an exhibition of the deoxidizing action of light rather than the effect of heat; the blow-pipe flame itself being scarcely visible, while the decomposing platinum, although necessarily of a lower temperature, is highly incandescent.

*Nov. 8, 1849.*

*Nov. 28  
1848*

A cubic inch of water at 62°, Bar. 30 inches, weighs in air 252.458 grains. The imperial gallon has been defined to contain



10 pounds avoirdupois (70,000 grains) of distilled water at that temperature and pressure. Its capacity is therefore 277.19 cubic inches. The specific gravity of water at 60° is 1, being the unit to which the densities of all other liquids and solids are conveniently referred; it is 815 times heavier than air at that temperature.

In its chemical relations water is eminently a neutral body. Its range of affinity is exceedingly extensive, water forming definite compounds, to all of which the name *hydrate* is applied, with both acids and alkalies, with a large proportion of the salts, and indeed with most bodies containing oxygen. It is also the most general of all solvents. Gay-Lussac has observed that the solution of a salt is uniformly attended with the production of cold, whether the salt be anhydrous or hydrated, and that, on the contrary, the formation of a definite hydrate is always attended with heat: a circumstance which indicates an essential difference between solution and chemical combination.\* Even the dilution of strong solutions of some salts, such as those of ammonia, occasions a fall of temperature. The solvent power of water for most bodies increases with its temperature. Thus, at 57° water dissolves one-fourth of its weight of nitre, at 92° one-half, at 131° an equal weight, and at 212° twice its weight of that salt. Solutions of such salts, saturated at a high temperature, deposit crystals on cooling. But the crystallization of some saturated solutions is often suspended for a time, in a remarkable manner, and afterwards determined by slight causes. Thus, if two pounds of crystallized sulphate of soda be dissolved in one pound of water, with the assistance of heat, and the solution be filtered while hot through paper, to remove foreign solid particles, and then set aside in a glass matrass, with a few drops of oil on its surface, it may become perfectly cold without crystallization occurring. Violent agitation even may not cause it to crystallize. But when any solid body, such as the point of a glass rod, or a grain of salt, is introduced into the solution, crystals immediately begin to form about the solid nucleus, and shoot out in all directions through the liquid. The solubility of many salts of soda and lime does not increase with the temperature, like that of <sup>most</sup> other salts.

Water is also capable of dissolving a certain quantity of air and other gases, which may again be expelled from it by boiling the water, or by placing it in vacuo. Rain-water generally affords 2½ per cent. of its bulk of air, in which the proportion of oxygen

2 bolts - hyd.  
Nitr. potash  
I dissolve one  
pure salt.

\* Ann. de Ch. et de Phys. t. lxx. p. 407. See also page 218 of this work.

gas is so high as 32 per cent., and in water from freshly melted snow 34.8 per cent., according to the observations of Gay-Lussac and Humboldt, while the oxygen in atmospheric air does not exceed 21 per cent. Boussingault finds that the quantity of air retained by water, at an altitude of 6 or 8000 feet, is reduced to one-third of its usual proportion. Hence it is that fishes cannot live in Alpine lakes, the air contained in the water not being in adequate quantity for their respiration. The following table exhibits the absorbability of different gases by water deprived of all its air by ebullition :—

100 cubic inches of water at 60° and 30 Bar., absorb of

	Dalton and Henry.	Saussure.
Hydrosulphuric acid	100 C. I.	253
Carbonic acid	100	106
Nitrous oxide	100	76
Olefiant gas	12.5	15.3
Oxygen	3.7	6.5
Carbonic oxide	1.56	6.2
Nitrogen	1.56	4.1
Hydrogen	1.56	4.6

The results of Saussure are probably nearest the truth for hydrosulphuric acid and nitrous oxide, but for the other gases those of Dalton and Henry are most to be depended on.

*Uses.*—Rain received after it has continued to fall for some time may be taken as pure water, excepting for the air it contains. But after once touching the soil, it becomes impregnated with various earthy and organic matters, from which it can only be completely purified by distillation. A copper still should be used for that purpose, provided with a copper or block tin worm, which is not used for the distillation of spirits, as traces of alcohol remaining in the worm and becoming acetic acid, cause the formation of acetate of copper, which would be washed out and contaminate the distilled water. The use of white lead cement about the joinings of the worm is also to be avoided, as the oxide of lead is readily dissolved by distilled water. The first portions ~~of the~~ distilled should be rejected, as they often contain ammonia, and the distillation should not be carried to dryness.

Water employed for economical purposes is generally submitted to a more simple process, that of filtration, by which it is rendered clear

and transparent by the removal of matter mechanically suspended in it. Such foreign matter may often be removed in a considerable degree by subsidence, on which account it is desirable that the water should stand at rest for a time, before being filtered. The filtration of liquids generally is effected, on the small scale, by allowing them to flow through unsized or filter paper, and that of water, on the large scale, by passing it through beds of sand. The sand preferred for that purpose is not fine, but gravelly, and crushed cinders or furnace clinkers may be substituted for it. Its function, as that also of the paper in the chemist's filter, is to act as a *support* for the finer particles of mud or precipitate which are first deposited on its surface, and form the bed that really filters the water. When the mud accumulates so as to impede the action of the sand filter, the surface of the sand is scraped, and an inch or two of it removed.

FIG. 104.

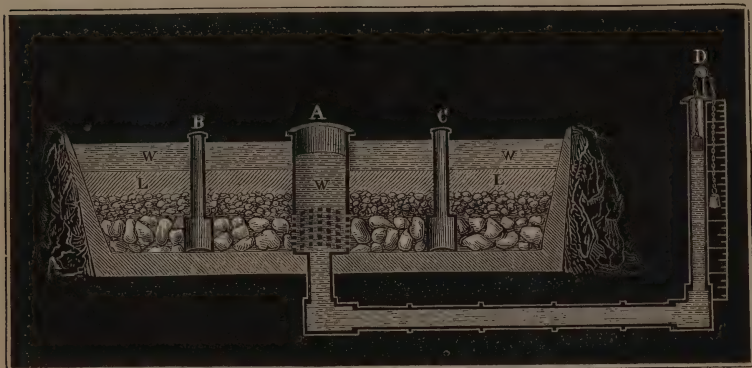


Fig. 104 is a section of the water-filter, as it is usually constructed for public works in Lancashire. An excavation of about six feet in depth, and of sufficient extent, is lined to a considerable thickness with well puddled clay, to make it water-tight. Upon the clay floor is laid first a stratum of large stones, then a stratum of smaller stones, and, finally, a bed of coarse sand or gravel, L L. To allow the air to escape from the lower beds, small upright tubes, open at both ends, B and C, are inserted in these beds, and rising above the surface of the water W W. The filtered water enters, from the lowest bed, into a large open iron cylinder A, the lower part of which is perforated for that purpose. The filtered water stands at the same height in the gauge tube D as in A; this height is observed by means of a float balanced by a weight which traverses a scale of feet and inches at D.

*Diagram 77.*

*Black's process.*

*Largest jar - add 3 lbs  
lime-water & stir  
well. Next day pass a  
portion thro' large thin paper filter*



Upward filtration through a bed of sand is sometimes practised, but it has the disadvantage that the filter cannot be cleaned in the manner indicated. Filtering under high pressure, and with great rapidity, has been practised in a very compact apparatus, consisting of a box, not above three feet square, filled with sand. This filter, which becomes speedily choked with the mud it detains, is cleansed by suddenly reversing the direction in which the water is passing through the box, which occasions a shock that has the effect of loosening the sand, and allowing the water to bring away the mud. The action of such a filter, erected at the Hôtel-Dieu of Paris, was favourably reported on by M. Arago\*.

Matter actually dissolved in water is not affected by filtration. No repetition of the process would withdraw the salt from sea-water and make it fresh. Hence the impregnation of peaty matter, which river water generally contains, and to the greatest extent in summer, when the water is concentrated by evaporation, is not removed by filtering. Animal charcoal is the proper substance for discolouring liquids, as it withdraws organic colouring matter, even when in a state of solution. *appears however to become insoluble and precipitate by the effect of filtration. Is also extracted or organic matter rapidly becomes nitrate filtering - K. Smith*

In the process of clarifying liquors by dissolving in them the white of egg and other albuminous fluids, the temperature is raised so as to coagulate the albumen, which thus forms a delicate net-work throughout the liquid, and is afterwards thrown up as scum in the boiling, carrying all the foreign matter suspended in the liquid along with it.

Gelatine, isinglass, or other "finings," added to wine in a turbid state, produce a precipitate with its tannin, which carries down all suspended matter; and on the settling of this precipitate, or its separation by filtering, the wine is found transparent.

The most usual earthy impurities in water, occasioning its hardness, are sulphate of lime, and the carbonate of lime dissolved in carbonic acid, both of which are precipitated on boiling the water, and occasion an earthy incrustation of the boiler. *the first of which is precipitated by evaporation*

So far as this precipitation is due to carbonate of lime it may be avoided by adding hydrochlorate of ammonia to the water, by which the lime is converted into chloride of calcium and becomes soluble. Water containing carbonate of lime may be also softened by the addition of lime-water, as recommended by Professor Clark. Thames water requires for this purpose the addition of about one-fourteenth *the last by means of the water at the boiler point*

\* Annales de Chim. et de Phys. t. lxx., p. 428.



of its bulk of lime-water. This action of lime-water will be explained under carbonic acid.

When waters contain iron, they are termed *chalybeate*: this metal is most frequently in the state of carbonate dissolved in carbonic acid, and rarely in a proportion exceeding one grain in a pound of water. The *sulphurous* waters, which are recognised by their peculiar odour, and by blackening silver and salts of lead, contain hydrosulphuric acid in a proportion not exceeding the usual proportion of air in spring water, and generally no oxygen. *Saline* waters for the most part contain various salts of lime and magnesia, and generally common salt. Their density is always considerably higher than that of pure water. *Sea-water* contains  $3\frac{1}{2}$  per cent. of saline matter, and has a density 1.0274. Its composition is interesting, as the sea comes to be the grand depository of all the soluble matter of the globe. A minute analysis of the water of the English Channel, executed by Mr. Schweitzer, is subjoined:—

Sea-water of the English Channel.		Grains.
Water		964.74372
Chloride of sodium		27.05948
———— potassium		0.76552
———— magnesium		3.66658
Bromide of magnesium		0.02929
Sulphate of magnesia		2.29578
———— lime		1.40662
Carbonate of lime		0.03301
		<hr/>
		1000.0000

In addition to those constituents, distinct traces of iodine and of ammonia were detected.\* According to Professor Forchhammer, the whole quantity of saline matter in water from different parts of the Atlantic varied from 35.7 parts (German sea) to 36.6 parts (tropics) in 1000 parts of the water. The relative proportion of the salts in the water of different seas varied very little.†

#### BINOXIDE OF HYDROGEN.

*Equivalent, 17, or 212.5 on Oxygen Scale; formula  $H + 2O$ , or  $HO_2$ .*

The second compound of hydrogen and oxygen is a liquid, con-

\* Phil. Mag. 3d Series, Vol. xv. page 58.

† Reports of the British Association, 1846, page 90.

taining twice as much oxygen as water, and is a body possessed of very extraordinary properties. It was discovered by Thenard, in 1818, who prepared it by a long and intricate process.

*Preparation.*—The formation of the binoxide of hydrogen depends upon the existence of a corresponding binoxide of barium. The latter is obtained by calcining pure nitrate of baryta at a high temperature in a porcelain retort, and afterwards exposing the earth baryta or protoxide of barium, which is left, in a porcelain tube heated to redness, to a stream of oxygen gas, which the protoxide rapidly absorbs, becoming binoxide. Treated with a little water the binoxide of barium slakes and falls to powder, forming a hydrate, of which the formula is  $\text{Ba O}_2 + \text{H O}$ . Dilute acids have a peculiar action upon this hydrate, which will be easily understood, if the binoxide of barium is represented as the protoxide united with an additional equivalent of oxygen, or as  $\text{Ba O} + \text{O}$ . They combine with the protoxide of barium, forming salts of baryta, and the second equivalent of oxygen, instead of being liberated in consequence, unites with the water of the hydrate, the HO of the preceding formula giving rise to  $\text{HO} + \text{O}$  or the binoxide of hydrogen, which dissolves in the water. Although it would be inconvenient to abandon the systematic name binoxide of hydrogen for this compound, still it must be allowed that the properties of the body, as well as its mode of preparation, are more favourable to the idea of its being a combination of water with oxygen, or *oxygenated water*, as it was first named by its discoverer, than a direct combination of its elements. It is recommended by Thenard to dissolve the binoxide of barium in hydrochloric acid considerably diluted with water, and to remove the baryta by sulphuric acid, which forms an insoluble sulphate of baryta. The hydrochloric acid, again free in the liquor, is saturated a second time with binoxide of barium, and precipitated; and after several repetitions of these two operations, the hydrochloric acid itself is removed by the cautious addition of sulphate of silver, and the sulphuric acid of the last salt by solid baryta. Such is an outline of the process, but its success requires attention to a number of minute precautions, which are fully detailed in the *Traité de Chemie* of the author quoted\*. The weak solution of binoxide of hydrogen, which this process affords, may be concentrated by placing it with a vessel of strong sulphuric acid under the receiver of an air-pump, until the solution attains a density of 1.452, when the

\* Vol. i. page 479 of the 6th edition.

binoxide itself begins to rise in vapour without change. It then contains 475 times its volume of oxygen.

M. Pelouze abridges this process considerably by employing hydrofluoric acid or fluosilicic acid, in place of hydrochloric acid, to decompose the binoxide of barium. By this operation, the baryta separates at once with the acid, in the state of the insoluble fluoride of barium, and nothing remains in solution but the binoxide of hydrogen. After thus decomposing several portions of binoxide of barium successively in the same liquor, the fluoride of barium may be separated by filtration, and the binoxide of hydrogen, which is still dilute, be concentrated by means of the air-pump.

*Properties.*—Binoxide of hydrogen is a colourless liquid resembling water, but less volatile, having a metallic taste, and instantly bleaching litmus and other organic colouring matters. It is decomposed with extreme facility, effervescing from escape of oxygen at a temperature of  $59^{\circ}$ , and when suddenly exposed to a greater heat, such as  $212^{\circ}$ , actually exploding from the rapid evolution of that gas. It is rendered more permanent by dilution with water, and still more so by the addition of the stronger acids, while alkalies have the opposite effect.

The circumstances attending the decomposition of this body are the most curious facts in its history. Many pure metals and metallic oxides occasion its instantaneous resolution into water and oxygen gas, by simple contact, without undergoing any change themselves, affording a striking illustration of catalysis (page 233); and this decomposition may excite an intense temperature, the glass tube in which the experiment is made sometimes becoming red hot. Some protoxides absorb at the same time a portion of the oxygen evolved, and are raised to a higher degree of oxidation, but most of them do not; and certain oxides, such as the oxides of silver and gold, are reduced to the metallic state, their own oxygen going off along with that of the binoxide of hydrogen. The decomposition of these metallic oxides cannot be ascribed to the heat evolved, for oxide of silver is reduced in a very dilute solution of the binoxide of hydrogen, although the decomposition is not then attended with a sensible elevation of temperature. The metallic oxides which are decomposed in this remarkable manner are originally formed by the decomposition of other compounds, and not by the direct union of their elements, which, in fact, exhibit little affinity for each other. In this general character they agree with binoxide of hydrogen itself.

*Uses.*—The binoxide of hydrogen is a substance which it is ex

ceedingly desirable to possess, with the view of employing it in bleaching, and for other purposes, as a powerful oxidating agent. But the expense and uncertainty of the process for preparing this compound have hitherto prevented any application of it in the arts, or even its occasional use as a chemical re-agent.

## SECTION III.

## NITROGEN.

*Synonyme, AZOTE. Equiv. 14, or 175 (O=100); symbol N; density 971.37; combining measure* □ □.

*For the tall jar I was dipping, have hint of scissors to prize up the cork. Low Ell. brother oxygen largest and Bell. jar & largest being stout, with Phosphorus. Lur N. & bottle oxygen Band le Dippin*

Dr. Rutherford, of Edinburgh, examined the air which remains after the respiration of an animal, and found that after being washed with lime-water, which removes carbonic acid, it was incapable of supporting either combustion or respiration. He concluded that it was a peculiar gas. Lavoisier afterwards discovered that this gas exists in the air of the atmosphere, forming indeed 4-5ths of that mixture, and gave it the name azote, (from  $\alpha$ , privative, and  $\zeta\omega\eta$  life), from its inability to support respiration. It was afterwards named nitrogen by Chaptal, because it is an element of nitric acid. Besides existing in air, nitrogen forms a constituent of most animal and of many vegetable substances. In a natural arrangement of the elements, nitrogen appears to have its place between oxygen and phosphorus (page 173).

*Preparation.*—Nitrogen is generally procured by allowing a combustible body to combine with the oxygen of a certain quantity of air confined in a vessel. For that purpose a little metallic or porcelain cup may be floated, by means of a cork, on the surface of the water-trough. A few drops of alcohol are then introduced into the cup, or a small piece of phosphorus is placed in it, and being kindled, a tall bell jar is held over the cup, with its lip in the water. The combustion soon terminates, and the water of the trough rises in the jar. Alcohol does not consume the oxygen entirely, a small portion of it still remaining mingled with the nitrogen; a certain quantity of carbonic acid gas is also produced by its combustion. But the combustion of phosphorus exhausts the oxygen completely, and leaves nitrogen unmixed with any other gas.

Nitrogen may be likewise conveniently obtained by conducting



*2 Strmg Amm. to 1 water Expt.*

chlorine gas into diluted ammonia. For delicate purposes of research this gas is best prepared by carrying air through a tube filled with reduced metallic copper in a pulverulent form, and heated to redness, by which the oxygen is entirely absorbed.

*Properties.*—Nitrogen gas is tasteless and inodorous; has never been liquefied, and is less soluble in water than oxygen. It is a little lighter than air, which possesses the mean density of 79.1 volumes of nitrogen and 20.9 volumes of oxygen. Nitrogen is a singularly inert substance, and does not unite directly with any other single element, so far as I am aware, under the influence of light or of a high temperature, unless, perhaps, oxygen and carbon. A burning taper is instantly extinguished in this gas, and an animal soon dies in it, not because the gas is injurious, but from the privation of oxygen, which is required in the respiration of animals. Nitrogen appears to be chiefly useful in the atmosphere, as a diluent of the oxygen, thereby repressing to a certain degree the activity of combustion and other oxidating processes. Of the fixation of free nitrogen ~~of~~ plants, there is no evidence. When heated with oxygen, nitrogen does not burn like hydrogen, nor undergo oxidation. But nitrogen may be made to unite with oxygen by transmitting several hundred electric sparks through a mixture of these gases in a tube, with water or an alkali present, and nitric acid is produced. The water formed by the combustion of hydrogen in air, or of a mixture of hydrogen and nitrogen in oxygen, has often an acid reaction, which is due to a trace of nitric acid. But when the hydrogen is mixed with air in excess, so as to prevent great elevation of temperature during the combustion, the oxidation of the nitrogen does not take place (Kolbe). Nitric acid is also a product of the oxidation of a variety of compounds containing nitrogen. Ammonia mixed with air, on passing over spongy platinum at a temperature of about  $572^{\circ}$ , is decomposed, and the nitrogen it contains is completely converted into nitric acid, by combining with the oxygen of the air. Cyanogen and air, under similar circumstances, occasion the formation of nitric and carbonic acids\*. Nitric acid is also largely produced by the oxidation of organic matters during putrefaction in air, when an alkali or lime is present, as in the natural nitre soils and artificial nitre beds.

A suspicion has always existed that nitrogen may be a compound body, but it has resisted all attempts to decompose it, and the evidence of its elementary character is equally good with that of most

\* Kuhlman, Phil. Mag. 3d Series, vol. xiv. page 157.

other bodies reputed simple. Before considering the compounds of nitrogen with oxygen, we may notice the properties of atmospheric air, which is regarded as a mechanical mixture of these gases.

*Diagram*

### THE ATMOSPHERE.

According to the new and most careful determination of the weight of air by M. Regnault, 100 cubic inches of atmospheric air, deprived of aqueous vapour and the small quantity of carbonic acid it usually contains, weigh ~~30.82926~~ grains, at 60° and 30 Bar. Its density at the same temperature and pressure is estimated at 1000, and is conveniently assumed as the standard of comparison for the densities of gaseous bodies, as water is for solids and liquids. Hence, at 62°, air is 810 times lighter than water, and 11,000 times lighter than mercury. The bulk of air varies with its temperature and the pressure affecting it, according to the same laws as other gases (pages 12 and 75)\*.

The mean pressure of the atmosphere at the surface of the sea is generally estimated as equal to the weight of a column of mercury of 30 inches in height, which is about 15 pounds on the square inch of surface, and is equivalent to a column of water of nearly 34 feet in height. The oxygen alone is equal to a column of 7.8 feet of water over the whole earth's surface, from which an idea may be formed of the immense quantity of that element, and how small the effect must be of the oxidating processes observed at the earth's surface in diminishing it. If the atmosphere were of uniform density, its height, as inferred from the barometer, would be 11,000

#### \* I. WEIGHT OF 1 LITER OF GASES, at 0° C., Bar. 0.76 meter (Regnault).

	In Grammes.
Atmospheric Air . . . . .	1.293187
Nitrogen . . . . .	1.256167
Oxygen . . . . .	1.429802
Hydrogen . . . . .	0.089578
Carbonic Acid . . . . .	1.977414

#### II. WEIGHT OF 100 CUBIC INCHES OF GASES; Bar. 29.92 inches.

	At 32° F. In Grains.	At 60° F. In Grains.	
32.706646 — Atmospheric Air . . . . .	32.58684	30.82926	at 60° F. in grains. 30.94071
31.763172 — Nitrogen . . . . .	31.66020	29.95260	30.00500
36.185013 — Oxygen . . . . .	36.18806	34.18079	34.33336
2.265402 — Hydrogen . . . . .	2.16216	2.04554	2.14321
50.007703 — Carbonic Acid . . . . .	50.03856	47.38972	47.31052

Here the French liter is taken at 61.028 English cubic inches; the gramme at 15.432 grains; and the volume of air and the other gases, at 60°, 1.05701, their volume at 32° being 1.

15.434

*39.37 inches*

*39.37 English inches = 3 ft, 3.37 inches*

times 30 inches, or 5.208 miles, but the density of air being proportional to the pressure upon it, diminishes with its elevation, the superior strata being always more rare and expanded than the inferior strata upon which they press.

## DENSITY OF THE ATMOSPHERE.

Height above the sea in miles.	Volume.
0	1
2.705	2
5.41	4
8.115	8
10.82	16
13.424	32
16.23	64

At a height of 2.705 miles (11,556 feet) the atmosphere is of half density, by calculation, or 1 volume is expanded into 2, and the barometer would stand at 15 inches; the density is again halved for every 2.7 miles additional elevation. From calculations founded on the phenomena of refraction, the atmosphere is supposed to extend, in a state of sensible density, to a height of nearly 45 miles. It is certainly limited, probably from the expansibility of the aerial particles having a natural limit (page 76). The atmospheric pressure also varies at the same place, from the effect of winds and other causes, which are not fully understood. Hence the use of the barometer as a weather glass; for wet and stormy weather is generally preceded by a fall of the mercury in the barometer, and fair and calm weather by its rise.

The temperature of the atmosphere is greatest at the earth's surface, and has been observed to diminish one degree for every 352 feet of ascent, in the lower strata. It is believed, however, that the progressive diminution is less rapid at great distances from the earth. But at a certain height, the region of perpetual congelation is attained even in the warmest climates; the summits of the Andes, which rise 21,000 feet, being perpetually covered with snow under the equator. The line of perpetual congelation, which has been fixed at 15,207 feet at 0° latitude, descends progressively in higher latitudes, being 3,818 feet at 60°, and only 1,016 feet at 75°. The decrease of temperature with elevation in the atmosphere is ascribed to two causes. 1. To the property which air has of becoming cold by expansion, which arises from an increase of its latent heat

*Dele*

with rarefaction. The actual temperature of the different strata of the atmosphere is indeed believed to be that due to their dilatation, supposing that they had all the same original temperature and density as the lowest stratum. 2. To the circumstance that the atmosphere derives its heat principally from contact with the earth's surface. The sun's rays appear to suffer little absorption in passing through the atmosphere; but there are some observations on the force of solar radiation which are not easily reconciled with that circumstance. A thermometer, of which the bulb is blackened, rises a certain number of degrees above the temperature of the air, when exposed to the sun, but the rise is decidedly greater on high mountains than near the level of the sea, and in temperate, or even arctic climates, which is more remarkable, than within the tropics. It is a question how solar radiation is obstructed in the hotter climates\*.

The blue colour of the sky has been found by Brewster to be due to light that has suffered polarization, which is therefore reflected light, like the white light of clouds. The air of the atmosphere must therefore have a disposition to absorb the red and yellow solar rays, and to reflect the blue rays. At great heights, the blue colour of the sky was observed by Theodore de Saussure to become deeper and deeper, being mixed with black, owing to the absence of white reflecting vapour or clouds. The red and golden tints of clouds appear to be connected with a remarkable property of steam observed by Professor J. Forbes. A light seen at night through steam issuing into the atmosphere from under a pressure of from 5 to 30 pounds on the inch, is found to appear of a deep orange red colour, exactly as if observed through a bottle containing nitrous acid vapour. The steam, when it possesses this colour, is mixed with air, and on the verge of condensation; and it is known that the golden hues of sunset depend upon a large proportion of vapour in the air, and are indeed a popular prognostic of rain.†

*Winds.*—The movement of masses of air, or wind, is always produced by inequality of temperature of the atmosphere at different points of the earth's surface, or in different regions of the atmosphere of equal elevation. The primary movement is always an ascending current, the heated and expanded air over some spot rising in a vertical column. Dense and colder air flows towards that point, pro-

\* Daniell's Meteorological Essays, 2d edit.

† Phil. Mag. 3d Series, vol. xiv. pp. 121 and 425, and vol. xv. pp. 25 and 419.

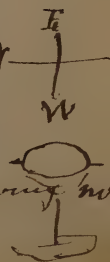
*Recommended Buff's Physics of the Globe.*



ducing the horizontal current which is remarked by an observer on the earth's surface. Some winds are of a very limited range, and depend upon local circumstances; such are the sea and land breeze experienced upon the coasts of tropical countries. From its low conducting power, the surface of the land is more quickly heated than the sea, so that soon after sunrise the expanded air over the former begins to ascend, and is replaced by colder air from the sea, forming the sea breeze. But after sunset, the earth's heat, being less in quantity, is more quickly dissipated by radiation than that of the sea, and the air over the land becomes dense and flows outwards, displacing the air over the sea, and producing the land breeze. It is obvious that these inferior currents must be attended by a superior current in an opposite direction, or that the air in these winds is carried in a perpendicular vortex of no great extent, of which the motion is reversed twice every twenty-four hours. A grand movement of a similar nature is produced in the atmosphere, from the high temperature of the equatorial compared with the polar regions of the globe; the air over the former constantly ascending, and having its place supplied by horizontal currents from the latter, within the lower region of the atmosphere. Hence, if the earth were at rest, the wind would constantly blow at its surface, from the poles to the equator, and in the opposite direction in the upper strata of the atmosphere. But the earth, accompanied by its atmosphere, makes a diurnal revolution upon its axis, in which any point on its surface is always passing to a point in space previously to the east of it, and with a velocity proportional to its circle of latitude on the globe; a velocity which is consequently nothing at the poles, and attains its maximum at the equator. The result of this is, that the lower current or polar stream, in tending to the equator, is constantly passing over parallels of latitude which have a greater degree of velocity of rotation to the east, than the stream itself, which comes thus to be felt as a resistance from the east; and instead of appearing as a wind directly from the north, as it really is, this stream appears as a wind from the east, with a certain northerly declination, which diminishes as the stream approaches the equator, where it flows directly from the east, constituting the great trade-wind which constantly blows across the Atlantic and Pacific Oceans from east to west within the tropics. Our keen east winds in spring have a low temperature, which attests their arctic origin. The upper or equatorial current has its course deflected by similar causes; starting from the equator it has a greater projectile force to the east than the parallels of latitude over which it has to pass, and

10  
*the S. wind  
 is wind from  
 the S.  
 a resistance  
 to the  
 air from the  
 east, which  
 but in this  
 current, not  
 certain in a  
 average but  
 only illustration*

*Move east on globe from pole to equator - having no  
 E. velocity appears a resistance from the East.  
 Pole globe eastward. George Mercator's projection.*



retaining this motion towards the east it appears, as it passes over them, a west wind or wind from the west. The upper current, flowing in the opposite direction from the trade-wind below, was actually experienced by Humboldt and Bonpland on the summit of the Peak of Teneriffe, and has been indicated at various times by the transport of volcanic ashes by its means.

These currents, instead of flowing in a uniform manner over and under each other, appear often to descend, and to flow side by side, giving rise to hot and cold seasons in their different courses, and the great variability of climate of the temperate zone. On the great oceans, within the temperate zone, westerly winds prevail greatly over easterly, which are supposed by some to be the upper current descending to the surface of the earth. These westerly winds temper the climate of the western sea-board both of Europe and America, which is much milder than the climate of their eastern coasts.

*omitted  
1845.  
since 1849*

The nature of the movement of the atmosphere in hurricanes has lately received considerable elucidation. It appears that they move in circles, and are great horizontal vortices, which are probably produced by currents of air meeting obliquely, like the little eddies or whirlwinds formed at the corner of streets. The whole vortex also travels, but its movement of translation is slow compared with its velocity of rotation.\*

Some hurricanes in the United States have a path of only a few hundred yards in width, but extending for many miles. An interesting theory of the origin of these, and many other local winds, has been proposed by Mr. Espy, and favourably reported upon by M. Babinet, to the French Institute. When a column of air, saturated with vapour at a high temperature, ascends in the atmosphere, it expands by the removal of pressure and becomes colder, as happens with dry air of the same temperature. But on being cooled to a certain point of temperature by its ascent, vapour condenses in the former, and raising the temperature of the column makes it specifically lighter and more buoyant. The ascent of damp air has thus a tendency to perpetuate itself, and may give rise to a most powerful upward aspiration, as is shewn by calculation, quite adequate to prostrate trees, and produce the mechanical effects observed; the whole funnel being carried over the surface of the earth by a more general movement of the atmosphere.

*Powerful  
aspiration  
produced.*

*Vapour.*—The properties of the atmosphere are much affected by

\* Colonel Reid on the Law of Storms; also the work of Mr. Espy.

the presence of watery vapour in it, which it acquires from contact with the surface of the sea, lakes, rivers, and humid soil. The quantity which can rise into the air is limited by its temperature (p. 90), and comes to be deposited again from various causes. The surface of the earth is cooled by radiation, and occasions the precipitation of dew from the air in contact with it. Vapour is also condensed into drops, from various agencies within the atmosphere itself. The following are the principal causes of clouds and rain. 1. The ascent of air in the atmosphere, and its consequent rarefaction, which is attended with cold. A cloud will be observed within the receiver of an air-pump, on the plate of which a little water has been spilt, on making two or three rapid strokes of the pump, which is due to this cause. It is observed in operation in the formation of the clouds and mists which settle on the summits of mountains. The wind passing over the surface of a level country is impeded by a mountain; rising in the atmosphere the stream overcomes the obstacle, and produces a cloud as it passes over the mountain, which appears stationary on its summit. 2. The mixing of opposite currents of hot and cold air, both saturated with humidity, may occasion rain, from the circumstance, first conjectured by Dr. Hutton, that the currents of air on mixing and attaining a mean temperature are incapable of sustaining the mean quantity of vapour. Thus, supposing equal volumes of air at  $60^{\circ}$  and  $40^{\circ}$ , both saturated with vapour, to be mixed, the tension of vapour at the former temperature being the 0.524th of an inch of mercury, and at the latter the 0.263rd of an inch, the mean tension is the 0.393rd of an inch. But the tension of vapour at  $50^{\circ}$ , the intermediate temperature is only the 0.375th of an inch; and consequently the excess of the former tension, or vapour of the 0.018th of an inch of tension, must condense as rain. But this is an inconsiderable cause of rain compared with the next. 3. Contact of air in motion with the cold surface of the earth, or mere proximity, appears to be the most usual cause of its refrigeration, and of the precipitation of rain from it. The mean temperature of January in this country is about  $34^{\circ}$ , but with a south-west wind the thermometer may be observed gradually to rise in the course of 48 hours to  $54^{\circ}$ . Now supposing this wind to be saturated with vapour at  $54^{\circ}$  and to be cooled to  $34^{\circ}$ , as it is on its first arrival, the moisture which it must deposit is very considerable, as will appear by the following calculation:—

Tension of vapour at $54^{\circ}$	0.429 inch.
„ „ at $34^{\circ}$	0.214 „

Condensed . . 0.215 „

Nov. 29, 1788.

*Air. Pump  
with black  
wet cloth, &  
jar already  
rings. Not  
the largest jar*

*The Cardinal  
points of the  
Compass  
chalked out  
to be uniform  
placed  
arranged.*



The mean annual fall of rain in London amounts to a column of 23 inches. The quantity collected by a rain-gauge is found to be affected to an extraordinary extent by very moderate differences of elevation. Thus the annual fall of rain in three situations was found, by Professor J. Phillips, to be as follows:—

	Inches.	Height.
Top of York Minster . . . . .	15.910	242 feet.
Roof of Museum . . . . .	20.461	73 "
Surface of ground . . . . .	24.401	0 " <i>One half m at the ground</i>

The last stated cause of rain throws some light on this inequality: the air is more cooled near the ground, and therefore deposits most humidity.

The annual fall is greater near the equator, and diminishes in high latitudes. At Granada (lat.  $12^{\circ}$  N.), it is 126 inches; at Calcutta (lat.  $19^{\circ} 46'$ ), 81 inches; Rome, 39 inches; average of England, 31 inches; St. Petersburg, 16 inches; Uleaborg,  $13\frac{1}{2}$  inches. The number of rainy days follows a different proportion, the average during the year being about as follows:—

In Northern Europe . . . . .	180
In Central Europe . . . . .	146
In Southern Europe . . . . .	120*

When clouds form at temperatures below  $32^{\circ}$ , the aqueous vapour is converted into an infinity of little needle-like crystals, which often diverge from each other at angles of

FIG. 105.

$60^{\circ}$  and  $120^{\circ}$ , as do also the thin crystals in freezing water. Snow differs very much in the arrangement of these spiculæ (fig. 105), but the flakes are all of the *same* configuration in the same storm. The figures are essentially referable to a hexagonal star or prism, one of the crystalline forms of ice. *Hail* is also produced by cold, but in circumstances which are entirely different. It occurs only in summer or in warm climates, and when the sun is above the horizon. It seems to be produced in a humid ascending current of air, greatly cooled by rarefaction, which has an upward velocity suffi-



\* See Müller's Physics and Meteorology, and Kämtz's Meteorology, by Walker.



# Weight of Atmosphere Air

1 Litre of dry air = 61.0271 cubic inches

Weight of Litre of air at  $32^{\circ}$  & 29.92 inches = 1.293187 grammes

(1 gramme = 15.438 grains) = 19.9642209 grains

100 cubic inches air at  $32^{\circ}$  & 29.92 inches = 32.713,697 grains

100 cubic inches air at  $32^{\circ}$  & 30 inches = 32.801,166 grains

1 cubic foot air at  $32^{\circ}$  & 30 inches = 566.804,1605 grains

+ 100 cubic inches air at  $60^{\circ}$  & 30 inches. = 30.948824 grains  
(Regnault)

Do ————— do. 31.0117 grains  
(Prout)

+ The expansion of air for every degree from  
 $32^{\circ}$  to  $212^{\circ}$  is calculated at  $\frac{1}{491}$  part

Dr. R. D. Thomson



Atmosphere

---

Clemente - Arctic &  
Lomid zone.

---









cient to sustain the falling hailstones at the same place till they attain considerable magnitude. The formation of hail is always attended with thunder or signs of electricity; and it has been found that small districts may be protected from its devastations by the elevation of many thunder rods.

*Analysis of air.*—A knowledge of the composition of the atmosphere followed that of its constituent gases. Various modes of analysis are practised:—1. A stick of phosphorus introduced into a known measure of air in a graduated tube, effects a complete absorption of the oxygen in 24 hours. On afterwards withdrawing the phosphorus the diminution of volume may be observed, which always indicates 20 or 21 per cent. of oxygen. 2. A known measure of air may be mixed with a slight excess of hydrogen more than sufficient to combine with its oxygen, 100 volumes of air, for example, with 50 volumes of hydrogen, and the mixture exploded in a strong glass tube of proper construction, by means of the electric spark. The diminution in volume of the gases after combustion is observed; and as oxygen and hydrogen unite in the exact ratio of one volume of the first to two volumes of the second, one-third of the diminution represents the volume of oxygen in the measure of air employed. The tube used for this purpose is called the voltaic eudiometer. The syphon eudiometer is a convenient instrument of this kind. It is formed of a straight tube moderately stout, of about 1-4th

Fig. 106.



or 3-8ths of an inch internal diameter, sealed at one end, and about 22 inches long. The closed end of this tube being softened by heat, two stout platinum wires are thrust through the glass from opposite sides of the tubes, so that their extremities in the tube approach within one-tenth of an inch of each other. These are intended for the transmission of the electric spark, and are retained, as if cemented, in the apertures of the glass when the latter cools. One-half the tube next the

closed end is afterwards graduated into hundredths of a cubic inch, and the tube is bent in the middle, like a syphon, as represented by *a* in the figure. By a little dexterity, a portion of the gaseous mixture to be exploded is transferred to the sealed limb of the instrument, at the water or mercurial trough, and the measure noted with the liquid at the same height in both limbs. The mouth of the open limb may then be closed by a cork, which can be fixed down by soft copper wire. A chain being now hung to one platinum

2 tubes.

The thin eudiometer only at present - 1853

2 Air + 1 H. unit & transformed into 2 bottles before hand.

at time to mix. Curial Transp. Take sparks from

much more. Syphon end; Coloured water.

Plain tube & Platinum balls.

Use large glass eudiometer

over mercury with watchman

cushion w/ pad.

Dr. H. have ready inserted in overman. try

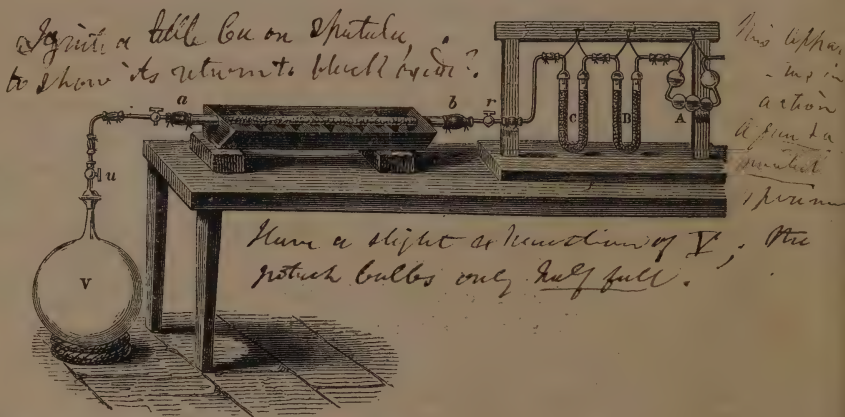
on the changes of climate in France: Huxley, Ann. Ch. 3 ser. XVI. 327.

wire, the other is presented to the prime conductor of an electric machine, or to the knob of a charged Leyden phial *b*, so as to take a spark through the mixture, which is thereby exploded. The risk of the tube being broken by the explosion, which is considerable in the ordinary form of the eudiometer, is completely avoided in this instrument by the compression of the air retained by the cork in the open limb, this air acting as a recoil spring upon the occurrence of the explosion in the other limb. 3. The combustion of the mixed gases may be determined without explosion by means of a little pellet of spongy platinum, and the experiment can then be conducted over mercury in an ordinary graduated tube. 4. Another exact method of removing oxygen from air, recommended by Gay-Lussac, is the introduction into the air of slips of copper moistened with hydrochloric acid, which absorb oxygen with great avidity.

5. A solution in ammonia of the subchloride of copper, or of any salt of the suboxide of that metal, such as the sulphite, absorbs oxygen with great avidity, and may be used in the analysis of air.

6. In the recent careful analyses of air by M. Dumas, the oxygen was withdrawn, by passing air over reduced metallic copper at red heat. To obtain the necessary precision in the results, the experiment was conducted in the following manner. In fig. 107, *a b* is

Fig. 107.



a tube of the difficultly fusible or hard glass used in organic analysis, which is filled with metallic copper (reduced from the black oxide of copper by hydrogen), and placed in a long trough furnace of sheet iron, in which it can be heated to redness throughout its whole length. The tube is provided with stopcocks at both ends, and at



tached by caoutchouc tubes to small glass tubes. By one of these small tubes it communicates with a glass balloon V, of about 1200 cubic inches in capacity, having a stopcock *u*; and by the other *r*, with a series of tubes A, B, and C. Of these A is a series of bulbs containing a concentrated solution of caustic potash, and is intended for the absorption of the small portion of carbonic acid present in air; the U shaped tube B contains fragments of pumice impregnated with the same alkaline solution; and the similar tube C is filled with pumice impregnated with oil of vitriol, in order to dry the air.

The balloon V is weighed and applied to the other <sup>end of the</sup> apparatus in a vacuous state. The tube *a b* containing the metallic copper is also weighed before hand. The tube and copper being heated to low redness, the stopcocks are partially opened, and air allowed to flow in a gradual manner into V. The oxygen is entirely absorbed by the copper, and the weight of that constituent ascertained by weighing the tube *a b* after the experiment. The nitrogen passes on alone into V, and its weight is found by again weighing that balloon. A great many analyses made in this way gave the following mean results:—

	Air by weight.	Air by volume.
Oxygen . . . . .	23.10	20.90
Nitrogen . . . . .	76.90	79.10
	<hr/> 100.00	<hr/> 100.00

Air from distant localities and different elevations has not exhibited any sensible variation in composition.

The theory of the constitution of mixed gases of Dalton supposes that the oxygen and nitrogen of air form independent atmospheres, the one gas not pressing upon or interfering with the other. If each of these atmospheres were of uniform density, their heights would obviously be inversely as the densities of the two gases, the height of the nitrogen column 8, and that of the oxygen 7; and the proportion of the one gas to the other would vary with the elevation. The same variation should occur in the atmosphere in its actual state: the proportion being supposed 21 per cent. at the level of the sea, by a calculation on this principle it should be 20.070 per cent. at a height of 10,000 Parisian feet, and 19.140 per cent. at a height of 20,000 feet. But as the influence of the great polar and equatorial currents is allowed to extend to a greater height in the atmosphere than the last, and than has ever been reached by man, it is not to be

*Nov. 20, 1848*

*p. 332  
Nov. 10, 1848*

*throughout the whole of the atmosphere*

*Method  
1848*

*\* Dalton on the Constitution of the Atmosphere. Phil. Mag. 1826, page 174.*

wondered at that no diminution in the proportion of oxygen is observable in the accurate analyses of air from the summit of the Faulhorn (8000 feet) which were lately made by Brunner, with the view of testing this hypothesis. \* *Note of double kind of Perm. - Lenz - CO<sub>2</sub>. After*

Besides these constituents, the atmosphere always contains a *forming* variable quantity of watery vapour and carbonic acid gas. The presence of the latter is observed by exposing to the air a bason of *CO<sub>2</sub> in* lime-water, which is soon covered by a pellicle of carbonate of lime. *26? times* Its proportion is ascertained by adding baryta-water of a known strength, from a graduated pipette, to a large bottle of the air to be examined; agitating after each addition, till a slip of yellow turmeric paper is made permanently brown by the baryta-water after agitation, which proves that more of the latter has been added than is neutralized by the carbonic acid of the air. The carbonic acid is in the equivalent proportion (by weight) of the quantity of baryta which has been neutralized. *Chlor. calcium with a few drops of ammoniac*

*Expt.* Another and perhaps more exact method is to draw a large but known volume of dry air through a U tube, containing pumice impregnated with caustic potash, and to pass it afterwards through a second U tube, containing oil of vitriol. The increase of weight on both tubes weighed together is the proportion of carbonic acid. *with more effective in absorbing CO<sub>2</sub>*

Like every subject connected with the atmosphere, the proportion of carbonic acid which it contains was ably investigated by the Saussures. The elder philosopher of that name detected the presence of this gas in the atmosphere resting upon the perpetual snows of the summit of Mont Blanc, so that there can be no doubt that carbonic acid is diffused through the whole mass of the atmosphere. The younger Saussure has ascertained, by a series of several hundred analyses of air, that the mean proportion of carbonic acid is 4.9 volumes in 10,000 volumes of air, or almost exactly 1 in 2000 volumes; but it varies from 6.2 as a maximum to 3.7, as a minimum in 10,000 volumes. Its proportion near the surface of the earth is greater in summer than in winter, and during night than during day upon an average of many observations. It is also rather more abundant in elevated situations, as on the summits of high mountains, than in the plains; a distribution of this gas which proves that the action of vegetation at the surface of the earth is sufficient to keep down the proportion of it in the atmosphere, within a certain limit.†

\* Poggendorff, Handwörterbuch der Chemie, Bd. i. S. 570.

† Saussure, Annales de Chim. et de Phys. t. xxxviii. p. 411; and t. xliv. p. 5.

An enormous quantity of carbonic acid is discharged from the elevated cones of the active volcanoes of America, according to the observations of Boussingault, which may partly account for the high proportion of that gas in the upper regions of the atmosphere. The gas emitted from the volcanoes of the old world, according to Davy and others, is principally nitrogen.

Carbonic acid is a constituent of the atmosphere which is essential to vegetable life, plants absorbing that gas, and deriving from it the whole of their carbon. Extensive forests, such as those of the Landes in France, which grow upon sands absolutely destitute of carbonaceous matter, can obtain their carbon in no other manner. But the oxygen of the carbonic acid is not retained by the plant, for the lignin and other constituent principles of vegetables, contain, it is well known, no more oxygen than is sufficient to form water with their hydrogen, and which, indeed, has entered the plant as water. The oxygen of the carbonic acid must therefore be returned in some form to the atmosphere. The discharge of pure oxygen gas from the leaves of plants was first observed by Priestley, and the general action of plants upon the atmosphere has subsequently been minutely studied by Sir H. Davy and Dr. Daubeny. The decomposition of carbonic acid requires the concurrence of light; and is not therefore sensible during the night. That plants fully compensate for the loss of oxygen occasioned by the respiration of animals and other natural processes is not improbable; but the mass of the atmosphere is so vast that any change in its composition must be very slowly effected. It has, indeed, been estimated that the proportion of oxygen consumed by animated beings in a century does not exceed 1-7200th of the whole quantity.

Other gases and vaporous bodies are observed to enter the atmosphere, but none of them can afterwards be detected in it, with the exception of hydrogen in some form, probably as the light carburetted hydrogen of marshes, of which Boussingault believes that he has been able to detect the presence of a minute but appreciable proportion.\* He also observed concentrated sulphuric acid to be blackened when exposed in a glass capsule to the air, protected from dust, and at a distance from vegetation, which he ascribes to the occasional presence in the air of some volatile carbonaceous compound which is absorbed and decomposed by the acid.

Ammonia ( $NH_3$ ) also is a minute but essential constituent of air, 1

\* Annales de Chim. et de Phys. lviii. 148.

1. One million parts of air contains 0.098 parts  $NH_3$  during day,  
equal to 0.283 carb. Ammonia.  
During night 0.169 & 0.474. The results are known to  
be slightly under the truth. Prussias.



*average of 2 phos-  
phate, HgCl, with  
aspirator. Kump  
Pondus White Hg*

probably in the form of carbonate. It is brought down by rain, and is the principal source of the nitrogen of plants. *By adding HCl to* Omitting the aqueous vapour always present in air, but of which the proportion is constantly fluctuating, it may be represented as follows, in 10,000 volumes:—

## COMPOSITION OF DRY AIR BY VOLUME.

Nitrogen . . . . .	7912
Oxygen . . . . .	2080
Carbonic acid . . . . .	4
Carburetted hydrogen (C H <sub>2</sub> ) . . . . .	4
Ammonia . . . . .	Trace

10,000

*it. Bolt. New  
office. The dew in  
the water in the air,  
any living room  
to. Boudinault  
blackening of SO<sub>2</sub>  
causes of—  
H<sub>2</sub>S;  
HCl, H<sub>2</sub>O.  
other vapours  
of course generally  
reason to believe  
one substance is  
the cause of chemical  
change.  
(1) If the true  
gaseous chem.  
substances, H<sub>2</sub>S,  
HCl, H<sub>2</sub>O.*

Of the odoriferous principles of plants, the miasmata of marshes and other matters of contagion, the presence, although sufficiently obvious to the sense of smell, or by their effects upon the human constitution, cannot be detected by chemical tests. *or rather, I doubt if* But it may be remarked in regard to them, that few or none of the compound volatile bodies we perceive entering the atmosphere, could long escape destruction from oxidation. The atmosphere contains, indeed, within itself the means of its own purification, and slowly but certainly converts all organic substances exposed to it into simpler forms of matter, such as water, carbonic acid, nitric acid, and ammonia. Although the occasional presence of matters of contagion in the atmosphere is not to be disputed, still it is an assumption, without evidence, that these substances are volatile or truly vaporous. (1) Other matters of infection with which we can compare them, such as the matter of cow-pox, may be dried in the air, and are not in the least degree volatile. (2) Indeed, volatility of a body implies a certain simplicity of constitution and limit to the number of atoms in its integrant particle, which true organic bodies appear not to possess. (3) Again, the source of such bodies being at all times inconsiderable, they would, if vapours, be liable to a speedy attenuation by diffusion so great as to render their action wholly inconceivable. It is more probable that matters of contagion are highly organized particles of fixed matter, which may find its way into the atmosphere, notwithstanding, like the pollen of flowers, and remain for a time suspended in it; a condition which is consistent with the admitted difficulty of reaching and destroying those bodies by gaseous chlorine, and with



the washing of walls and floors as an ordinary disinfecting practice. On this obscure subject, I may refer to a valuable paper by the late Dr. Henry upon the application of heat to disinfection, in which it is proved that a temperature of  $212^{\circ}$  is destructive to such contagious matters as could be made the subject of experiment.\*

With reference to gaseous disinfectants, it may be remarked that sulphurous acid gas (obtained by burning sulphur) is preferable, on speculative grounds, to chlorine. No agent checks more effectually the first development of animal or vegetable life. This it does by preventing oxidation. In the same manner it renders impossible the first step in putrefactive decomposition and fermentation. All animal odours and emanations are most immediately and effectively destroyed by it. The fœtid odour from the boiling solution of cochineal (for instance), which is so persistent in dye-houses, is most completely removed by the admission of sulphurous acid vapour (J. Graham).

The compounds of nitrogen with oxygen are the following:—  
 Protoxide of nitrogen or nitrous oxide . . . . . NO  
 Binoxide of nitrogen or nitric oxide . . . . . NO<sub>2</sub>  
 Nitrous acid . . . . . NO<sub>3</sub>  
 Peroxide of nitrogen (hyponitric acid of Thenard) . . . . . NO<sub>4</sub>  
 Nitric acid . . . . . NO<sub>5</sub>

#### PROTOXIDE OF NITROGEN.

*Syn.* PROTOXIDE OF AZOTE, NITROUS OXIDE; *Eq.* 22 or 275; NO; density 1520·4;   .

This gas was discovered by Dr. Priestley about 1776, and studied by Davy, whose "Researches, Chemical and Philosophical," published in 1809, contain an elaborate investigation of its properties and composition. Davy first observed the stimulating power of nitrous oxide when taken into the lungs, a property which has since attracted a considerable degree of popular attention to this gas.

*Preparation.*—Protoxide of nitrogen is always prepared from the nitrate of ammonia. Some attention must be paid to the purity of that salt, which should contain no hydrochlorate of ammonia. It is formed by adding pounded carbonate of ammonia to pure nitric acid,

\* Phil. Mag. 2d Series, vol. x. p. 363, and vol. xi. pp. 22, 207 (1832).

which, if concentrated, may be previously diluted with half its bulk of water, so long as there is effervescence; and a small excess of the carbonate may be left at the end in the liquor. The solution should be filtered, and concentrated till its boiling point begins to rise above  $250^{\circ}$ , and a drop of it becomes solid on a cool glass plate. On cooling, it forms a solid cake, which may be broken into fragments. To obtain nitrous oxide, a quantity of this salt, which should never be less than 6 or 8 ounces, is introduced into a retort, or

FIG. 108.



a globular flask, called a bolt-head *a*, and heated by a charcoal choffer *b*, the diffused heat of which is more suitable than the heat of a lamp. Paper may be pasted over the cork of the bolt-head to keep it air-tight. At a temperature not under  $340^{\circ}$  the salt boils and begins to undergo decomposition, being resolved into nitrous oxide and water. As

heat is evolved in this decomposition, which is a kind of combustion or deflagration, the choffer must be withdrawn to such a distance from the flask as to sustain only a moderate ebullition. If the temperature is allowed to rise too high, the ebullition becomes tumultuous, and the flask is filled with white fumes, which have an irritating odour; and the gas which then comes off is little more than nitrogen. Nitrous oxide should be collected in a gasometer or in a gas-holder filled with water of a temperature about  $90^{\circ}$ , as cold water absorbs much of this gas. The whole salt undergoes the same decomposition, and nothing whatever is left in the retort.\*

Nitrous oxide is likewise produced when the salt called nitrosulphate of ammonia is thrown into an acid; and also when zinc and tin are dissolved in dilute nitric acid, but the latter processes do not afford the gas in a state of purity.

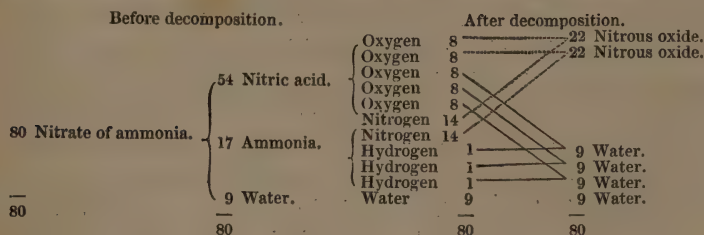
The nature of the decomposition of the nitrate of ammonia will be best explained by the following diagram, in which an equivalent of the salts, or 80 parts, is supposed to be used. It will be observed that the three equivalents of hydrogen in the ammonia are burned,

\* For the preparation and properties of this and other gases, the Elements of Chemistry (1829) of the late Dr. Henry may still be consulted with advantage.

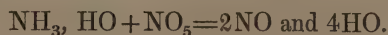
*Deflagration*  
*an hot cake*  
*1. gentle in bottle*  
*2. Sulphuric acid*  
*in bottle*  
*3. Charcoal with*  
*in round*  
*4. Phosphorus*  
*in round*

*Try ed with first*

or combine with three equivalents of the oxygen of the nitric acid, and form water, while the two equivalents of nitrogen in the ammonia and nitric acid combine with the two remaining equivalents of the oxygen of the latter :—



Or in symbols :—



From the diagram it appears that 80 grains of the salt yield 44 grains of nitrous oxide and 35 grains of water. One grain of salt yields rather more than one cubic inch of gas.

*Properties.*—Nitrous oxide possesses the usual mechanical properties of gases, and has a faint agreeable smell. It has been liquefied by evolving it from the decomposition of the nitrate of ammonia in a sealed tube, and possessed in the liquid state an elastic force of above 50 atmospheres at 45°. The gas is formed by the union of a combining measure, or 2 volumes of nitrogen, with a combining measure, or 1 volume of oxygen, which are condensed into 2 volumes, the combining measure of this gas. The weight of a single volume, or the density of the gas, is therefore by calculation—

$$\frac{971.4 + 971.4 + 1105.6}{2} = 1524.2$$

Cold water agitated with this gas dissolves about three-fourths of its volume of the gas, and acquires a sweetish taste, but, I believe, no stimulating properties. Bodies which burn in air, burn with increased brilliancy in this gas, if introduced in a state of ignition. A newly blown out taper with a red wick may be rekindled in it, as in oxygen. Mixed with an equal bulk of hydrogen, and ignited by flame and the electric spark, it detonates violently. In all these cases of combustion, the nitrous oxide is decomposed, its oxygen uniting with the combustible and its nitrogen being set free. When transmitted through a red-hot porcelain tube, nitrous oxide is likewise decomposed and resolved into oxygen, nitrogen, and the peroxide of nitrogen.

*W. H. W. Charles's*  
*W. H. W. Charles's*  
*bottles -*

Nitrous oxide was supposed by Davy to combine with alkalies, when generated in contact with them, but these compounds have since been found to contain nitrosulphuric acid.

This gas may be respired for two or three minutes without inconvenience, and when the gas is unmixed with air, and the lungs have been well emptied of air before respiring, it induces an agreeable state of reverie or intoxication, often accompanied with considerable excitement, which lasts for a minute or two, and disappears without any unpleasant consequences. The gas from an ounce and a half or two ounces of nitrate of ammonia is sufficient for a dose, and it should be respired from a bag of the size of a large ox-bladder, and provided with a wooden tube of an inch internal diameter. The volume of the gas diminishes rapidly during the inspiration, and finally only a few cubic inches remain. An animal entirely confined in this gas soon dies from the prolonged effects of the intoxication.

#### BINOXIDE OF NITROGEN.

*Syn.* BINOXIDE, OR DEUTOXIDE OF AZOTE, NITRIC OXIDE.

*Eq.* 36 or 375;  $\text{NO}_2$ ; *density* 1038.8;



This gas, which comes off during the action of nitric acid upon most metals, appears to have been collected by Dr. Hales, the father of pneumatic chemistry, but its properties were first minutely studied by Dr. Priestley.

*Preparation.*—Binoxide of nitrogen is easily procured by the action of nitric acid diluted to the specific gravity 1.2, upon sheet copper clipped into small pieces. As no heat is required, this gas may be evolved like hydrogen from a gas bottle (page 307). Mercury may be substituted for copper, but it is then necessary to apply a gentle heat to the materials. This gas may be collected and retained over water without loss.

In dissolving in nitric acid, the copper takes oxygen from one portion of acid and becomes oxide of copper, which combines with another portion of acid, and forms the nitrate of copper, the solution of which is of a blue colour. The portion of nitric acid which is decomposed losing three equivalents of oxygen and retaining two, appears as nitric oxide gas. This is more clearly shown in the following diagram:—



## ACTION OF NITRIC ACID UPON COPPER.

Before decomposition.			After decomposition.	
54 Nitric acid	Nitrogen	14	30 Binoxide of nitrogen.	
	Oxygen	8		
	Oxygen	8		
	Oxygen	8		
	Oxygen	8		
32 Copper	Copper	32	94 Nitrate of copper.	
54 Nitric acid	Nitric acid	54		
32 Copper	Copper	32		
54 Nitric acid	Nitric acid	54		
32 Copper	Copper	32		
54 Nitric acid	Nitric acid	54	94 Nitrate of copper.	
<hr/> 312		<hr/> 312	<hr/> 312	

Or in symbols :—



*Properties.*—This gas is colourless, but when mixed with air it produces ruddy fumes of the peroxide of nitrogen. It is irritating, and causes the glottis to contract spasmodically when an attempt is made to respire it. Nitric oxide has never been liquefied: water at  $60^\circ$ , according to Dr. Henry, takes up only 5 or 6 per cent. of this gas. It is formed of one combining measure of nitrogen or 2 volumes, and two combining measures of oxygen or 2 volumes, united without condensation, so that the combining measure of nitric oxide contains 4 volumes. The weight of one volume, or the density of the gas, is therefore

$$\frac{971.4 + 971.4 + 1105.6 + 1105.6}{4} = 1038.5.$$

This gas is not decomposed by a low red heat.

Many combustibles do not burn in nitric oxide, although it contains half its volume of oxygen. A lighted candle and burning sulphur are extinguished by it; mixed with hydrogen, it is not exploded by the electric spark or by flame, but it imparts a green colour to the flame of hydrogen burning in air. Phosphorus and charcoal, however, introduced in a state of ignition into this gas, continue to burn with increased vehemence. The state of combination of the oxygen in this gas appears to prevent that substance from uniting with combustibles, unless, like the two last mentioned, they evolve

continued to burn.

no ex-  
inquiries

element

substance

so much heat as to decompose the nitric oxide. Several of the more oxidable metals, such as iron, withdraw <sup>one</sup> ~~the~~ half of the oxygen from this gas, when left in contact with it, and convert it into nitrous oxide.

No property of nitric oxide is more remarkable than its attraction for oxygen, and it may be employed to separate this from all other gases. Nitric oxide indicates the presence of free oxygen in a gaseous mixture, by the appearance of fumes which are pale and yellow with a small, and reddish brown and dense with a large proportion of the latter gas; and also by a subsequent contraction of the gaseous volume, arising from the absorption of these fumes by <sup>water</sup> ~~the~~ <sup>for mercury</sup> water. Added in sufficient quantity, nitric oxide will thus withdraw <sup>or bottle</sup> ~~the~~ oxygen most completely from any mixture. But notwithstanding this property, nitric oxide cannot be employed with advantage in the analysis of air or similar mixtures, for the contraction which it occasions does not afford certain data for determining the proportion of oxygen which has disappeared. Nitric oxide is capable of combining with different proportions of oxygen, a combining measure or 4 volumes of the gas uniting, in such experiments, with 1, 2 or 3 volumes of oxygen, and forming nitrous acid, peroxide of nitrogen or nitric acid, or several of these compounds at the same time.

This oxide of nitrogen, like the preceding, is a neutral body, and has a very limited range of affinity. A substance is left on igniting the nitrate of potash or baryta, which was supposed to be a compound of nitric oxide with potassium, or barium, but Mitscherlich finds it to be either the caustic protoxide itself or the peroxide of the metal. But nitric oxide is absorbed by a solution of the sulphate of iron, which it causes to become black; the greater part of the gas may be expelled again by boiling the solution. All the soluble proto-salts of iron have the same property, and the nitric oxide remains attached to the oxide of iron when precipitated in the insoluble salts of that metal. The proportion of nitric oxide in these combinations is found by Peligot to be definite; one eq. <sup>of the</sup> ~~of the~~ nitric oxide to four <sup>eq.</sup> ~~of the~~ of the protoxide of iron; or, the nitric oxide contains the proportion of oxygen required to convert the protoxide into sesquioxide of iron.\* Nitric oxide is also absorbed by nitric acid. With sulphurous acid nitric oxide forms a compound which will be more particularly noticed under that acid.

\* Annales de Chim. et de Phys. t. liv. p. 17.

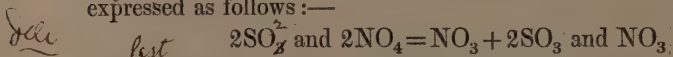
## NITROUS ACID.

*Syn.* AZOTOUS ACID (*Thenard*). *Eq.* 38 or 475;  $\text{NO}_3$ .

The direct mode of forming this compound is by mixing 4 volumes of binoxide of nitrogen with 1 volume of oxygen, both perfectly dry, and exposing the mixture to a great degree of cold. The gases unite, and condense into a liquid of a green colour, which is very volatile, and forms a deep reddish yellow coloured vapour. Nitrous acid prepared in this way is decomposed at once when thrown into water; an effervescence occurring, from the escape of nitric oxide, and nitric acid being produced, which gives stability to a portion of the nitrous acid. Nitrous acid cannot be made to unite directly with alkalies and earths, probably owing to the action of water first described. But when oxygen gas is mixed with a large excess of nitric oxide, in contact with a solution of caustic potash, the gases were found by Gay-Lussac always to disappear in the proportions of nitrous acid, which was produced and entered into combination with the potash, forming a *nitrite* of potash. Similar nitrites may also be produced by calcining the nitrate of soda till the fused salt becomes alkaline; or by boiling the nitrate of lead with metallic lead. The nitrite of soda may be dissolved and filtered, and the solution precipitated by nitrate of silver; a process which gives the nitrite of silver, a salt possessing a sparing degree of solubility, like that of cream of tartar, but which may be purified by solution and crystallization, and then affords ready means of obtaining the other nitrites by double decomposition (*Mitscherlich*). Nitrous acid is liberated from the nitrites by acetic acid. When free sulphuric acid is added to a solution of nitrite of silver, the disengaged nitrous acid is immediately resolved into nitric acid and nitric oxide. The subnitrite of lead, on the other hand, may be decomposed by the bisulphate of potash or soda to obtain a neutral nitrite of one of these bases (*Berzelius*). The nitrites of potash and soda are soluble in alcohol, while the nitrates are not so.

Nitrous acid is also capable of combining with several acids, in particular with iodic, nitric, and sulphuric acids. Its combination with the last is obtained by sealing up together liquid sulphurous acid and peroxide of nitrogen ( $\text{NO}_4$ ) in a glass tube. In the course of a few days the tube may be opened: the substances <sup>then the</sup> ~~are~~ combined,

*test.* and form a solid mass, which may be heated up to  $(200^{\circ} \text{C.})$  its point of fusion. At a higher temperature it distils without alteration. In this experiment, sulphurous acid acquires an equivalent of oxygen, and becomes sulphuric acid, while peroxide of nitrogen loses an equivalent of oxygen, and becomes nitrous acid, but one half only of the latter acid formed unites with sulphuric acid, the composition of the body formed being  $\text{NO}_3 + 2\text{SO}_3$ . The reaction is expressed as follows:—



This <sup>*best*</sup> compound is soluble in strong oil of vitriol without decomposition; but from sulphuric acid somewhat diluted it takes water, and forms a crystalline substance, which often appears in the manufacture of sulphuric acid, as ~~we~~ shall afterwards <sup>*be found*</sup> find. The original solid compound is decomposed by pure water or highly diluted sulphuric acid, and the sulphuric and nitrous acids become free. The tendency of nitrous acid to combine with other acids has already been noticed, as assimilating this compound of nitrogen to arsenious acid and the oxide of antimony (page 172).

#### PEROXIDE OF NITROGEN.

*Syn.* HYPONITRIC ACID, NITROUS GAS (*Berzelius*). *Eq.* 46 or 575;

$\text{NO}_4$ ; *theoretical density*, 1591.3;

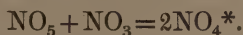

This compound forms the principal part of the ruddy fumes which always appear on mixing nitric oxide with air. As it cannot be made to unite either directly or indirectly with bases, and has no acid properties, any designation for this oxide of nitrogen which implies acidity should be avoided, and the name nitrous acid in particular, which is applied on the continent to the preceding compound. The name peroxide of nitrogen is more in accordance with the rules generally followed in naming such compounds.

*Preparation.*—When 4 volumes of nitric oxide and 2 of oxygen, both perfectly dry, are mixed, this compound is alone produced, and the six volumes of mixed gases are condensed into 4 volumes, which may be considered the combining measure of peroxide of nitrogen. The weight of 1 volume, or the density of this gas, must therefore be

$$\frac{1038.5 \times 4 + 1105.6 \times 2}{4} = 1591.3.$$



The peroxide of nitrogen is also contained in the coloured and fuming nitric acid of commerce, and may be obtained in the liquid condition by gently warming that acid, and condensing the vapour which comes over, by transmitting it through a glass tube surrounded by ice and salt. But it is prepared with most advantage from the nitrate of lead, the crystals of which, after being pounded and well dried, to deprive the salt of hygrometric water, are distilled in a retort of hard glass, or porcelain, at a red heat, and the red vapours condensed in a receiver kept very cold by a freezing mixture. Oxygen gas escapes during the whole process, the nitric acid of the nitrate of lead being resolved into oxygen and peroxide of nitrogen; or  $\text{NO}_5 = \text{NO}_4$  and  $\text{O}$ . As obtained by the last process, which was proposed by Dulong, peroxide of nitrogen is a highly volatile liquid, boiling at  $82^\circ$ , of a red colour at the usual temperature, orange yellow at a lower temperature, and nearly colourless below zero, of density 1.451, and a white solid mass at  $-40^\circ$ . It is exceedingly corrosive, and, like nitric acid, stains the skin yellow. The red colour of its vapour becomes paler at a low temperature, but with heat increases greatly in intensity, so as to appear quite opaque when in a considerable body at a high temperature. It is the vapour which Brewster observed to produce so many dark lines in the spectrum of a ray of light which passes through it (page 106). The peroxide is not decomposed by a low red heat, and appears to be the most stable of the oxides of nitrogen. No compound of it is known, unless peroxide of nitrogen be the radical, as some suppose, of nitric acid. But Berzelius is inclined to consider this oxide as itself a compound of nitric and nitrous acids, for



The liquid peroxide of nitrogen is partially decomposed by water, nitric oxide coming off with effervescence, and more and more nitric acid being produced, in proportion to the quantity of water added; but a portion of the peroxide always escapes this action, being protected by the nitric acid formed. In the progress of this dilution the liquid undergoes several changes of colour, passing from red to yellow, from that to green, then to blue, and becoming at last colourless. The peroxide of nitrogen is readily decomposed by the more oxidable metals, and is a powerful oxidizing agent.


\* *Traité de Chimie*, par J. J. Berzelius, traduite par MM. Esslinger et Hoeffer, Didot, Paris, 1845. An excellent edition of this most valuable system of chemistry.

*Dec. 5, 1848, in  
closing process for NO<sub>5</sub>.*

*Dec. Nov. 22, 1848. A. 352*

## NITRIC ACID.

*Syn.* AZOTIC ACID (*Thenard*). *Eq.* 54 or 675;  $\text{NO}_5$ ; does not exist except in combination.



A knowledge of this highly important acid has descended from the earliest ages of chemistry, but its composition was first ascertained by Cavendish, in 1785. He succeeded in forming nitric acid from its elements, by transmitting a succession of electric sparks during several days through a small quantity of air, or through a mixture of 1 volume of nitrogen and  $2\frac{1}{2}$  volumes of oxygen, confined in a small tube over water, or over solution of potash; in the last case, the absorption of the gases was complete, and nitrate of potash was obtained. A trace of this acid in combination with ammonia has been detected in the rain of thunder-storms, produced probably in the same manner. It was also observed by Gay-Lussac to be the sole product when nitric oxide is added, in a gradual manner, to oxygen in excess over water; the gases then unite, and disappear in the proportion of 4 volumes of the former to 3 of the latter. It is also a constituent of the salt, nitre or saltpetre, found in the soil of India and Spain, which is a nitrate of potash, and also of nitrate of soda, which occurs in large quantities in South America.

*Preparation.*—This acid <sup>was supposed to be incapable of</sup> cannot exist in an insulated state, but is always in combination with water, as in aqua fortis or the hydrate of nitric acid, or with a fixed base, as in the ordinary nitrates. The hydrate, (which is popularly termed nitric acid,) is eliminated from nitrate of potash by means of oil of vitriol, which is itself a hydrate of sulphuric acid. That acid unites with potash, in this decomposition, and forms sulphate of potash, displacing nitric acid, which last brings off in combination with itself the water of the oil of vitriol. There is a great advantage, first pointed out by <sup>Mr. R. Phillips,</sup> in using two equivalents of oil of vitriol to one of nitrate of potash, which is 97 of the former to 100 of the latter, or nearly equal weights. The acid and salt, in these proportions, are introduced into a capacious plain retort, provided with a flask as a receiver. Upon the application of heat, a little of the nitric acid first evolved undergoes decomposition, and red fumes appear, but soon the vapours become nearly colourless, and are easily condensed in the receiver. During the whole distillation, the temperature need not exceed  $260^\circ$ . The mass remains pasty till all the nitric acid is disengaged, and then

*Mr. Anhydrous*  
*totally uncombined*  
*a highly volatile*  
*crystalline solid*  
*by J. H. D. D. D.*

*Process*  
*16 oz Nitric*  
*acid*  
*33.3 Meas H<sub>2</sub>O*  
*give 9 1/2 oz H<sub>2</sub>O*  
*about 100*  
*of the acid*  
*with fumes*  
*& sandstone as*  
*in Ph arm.*  
*p. 73.*

enters into fusion; red vapours again appearing towards the end of the process. The residuary salt is the bisulphate of potash, or double sulphate of water and potash,  $\text{HO.SO}_3 + \text{KO.SO}_3$ . The rationale of this important process is exhibited in the following diagram:—

## PROCESS FOR NITRIC ACID.

*Diagram*

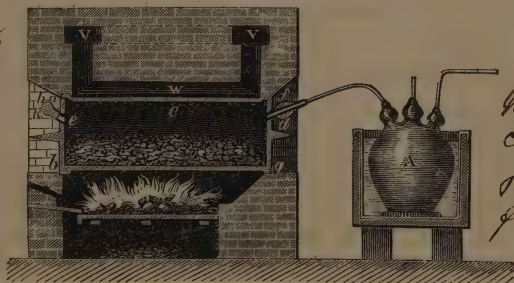
Before decomposition.		After decomposition.	
101 Nitrate of potash.	{ Nitric acid . 54	63 Nitric acid and water.	
	{ Potash . . 47		
49 Oil of vitriol.	{ Water . . 9		
49 Oil of vitriol.	{ Sulphuric acid 40	87 Sulphate of potash } bisul. of	
	{ Oil of vitriol . 49	49 Sulphate of water. } potash.	
199	199	199	

In this operation twice as much sulphuric acid is employed as is required to neutralize the potash of the nitre, by which means the whole nitric acid is eliminated without loss at a moderate temperature, and a residuary salt is left which is easily removed from the retort.

With half the preceding quantity, or a single equivalent of oil of vitriol, the materials in the retort are apt to undergo a vesicular swelling, upon the application of heat, and to pass into the receiver. Abundance of ruddy fumes are also evolved, that are not easily condensed, and prove that ~~the~~ nitric acid is decomposed. The temperature in this process must also be raised inconveniently high towards the end of the operation, in order to decompose the whole nitre. The peculiarities of the decomposition here arise from the formation of bisulphate of potash in the operation, the whole sulphuric acid uniting in the first instance with half the potash of the nitre. Now, it is only at an elevated temperature that the acid salt thus formed can decompose the remaining nitre;—a temperature which is

FIG. 109.

sufficient to decompose nitric acid, as may be proved by transmitting the vapour of the concentrated acid through a tube heated to the same degree.





Ordinary nitric acid for manufacturing purposes is generally prepared by distilling nitrate of soda with an equivalent of sulphuric acid not at its highest degree of concentration in a large cylinder of cast iron *c* (fig. 109, page 347), supported in brickwork over a fire. Both ends of the cylinder are moveable, and generally consist of circular discs of stone. The nitric acid which distils over is condensed in a series of large vessels of salt-glaze ware, of the form of Woulf bottles, of which one, *X*, is shewn in the figure.<sup>109</sup>

*A* The iron cylinders are generally so supported that two of them are heated by one fire, as in fig. 110, which is a sectional view of three pairs of such retort cylinders. The iron of the vault or roof of the cylinder is most apt to be corroded by the acid vapours, and is therefore protected by a coating of fire-clay or of tiles of the same material cemented together.

Fig. 110.



*Properties.*—The acid prepared by the first process is colourless, or has only a straw yellow tint. If the oil of vitriol has been in its most concentrated condition, which is seldom the case, the nitric acid is in its state of highest concentration also, and contains no more than a single equivalent of water. The density of this acid is 1.522 at 58°; but a slight heat disengages a little peroxide of nitrogen from it, and its density becomes 1.521 (Mitscherlich).<sup>1.521</sup> The density of the strongest colourless nitric acid which Mr. Arthur Smith could prepare was 1.517 at 60°; it boiled at 184°, and came within 1 per cent. of the protohydrate in composition, (Chem. Mem. iii, 402). When distilled, it is partially decomposed by the heat, and affords a product of a strong yellow colour. Its vapour transmitted through a porcelain tube, heated to dull redness, is decomposed in a great measure into oxygen and peroxide of nitrogen; and into oxygen and nitrogen gases, when the tube is heated to whiteness. The colourless liquid acid becomes yellow, when exposed to the rays of the sun, and on loosening the stopper of the bottle it is sometimes projected with force, from the state of compression of the disengaged oxygen. Hence to preserve this acid colourless it must be kept in a covered bottle. It congeals at about -40°, but diluted with half its weight of water, it becomes



solid at  $1\frac{1}{2}^{\circ}$ , and with a little more water its freezing point is again lowered to  $-45^{\circ}$ . Exposed to the air, the concentrated acid fumes, from the condensation by its vapour of the moisture in the atmosphere. It also attracts moisture from damp air, and increases in weight; and when suddenly mixed with 3-4ths of its weight of water, may rise in temperature from  $60^{\circ}$  to  $140^{\circ}$ .

Nitric acid has a great affinity for water, and diminishes in density with the proportion of water added to it. A table has been constructed in which the per centage of absolute acid is expressed in mixtures of various densities, which is useful for reference and will be given in an appendix. There appears to be no definite hydrate of this acid between the first (the nitrate of water), and that containing 3 eq. of water additional (A. Smith). The first has no action upon tin or iron. The second is acid of density 1.424, which therefore contains 4 eq. of water. This last hydrate was found by Dr. Dalton to have the highest boiling point of any hydrate of nitric acid: it is  $250^{\circ}$ , and both weaker and stronger acids are brought to this strength by continued ebullition, the former losing water and the latter acid. The density of the vapour of this hydrate is found to be 1243 by A. Bineau, and it contains 2 volumes of nitrogen, 5 volumes of oxygen, and 8 volumes of steam condensed into 10 volumes, which are therefore the combining measure of this vapour.\*

Nitric acid is exceedingly corrosive, and one of the strongest acids, yielding only in that respect to sulphuric acid. The facility with which it parts with its oxygen renders it very proper for oxidating bodies in the humid way, a purpose for which it is constantly employed. Nearly all the metals are oxidized by means of it; some of them with extreme violence, such as copper, mercury, and zinc, when the concentrated acid is used; and tin and iron by the acid very slightly diluted. Poured upon red hot charcoal, it causes a brilliant combustion. When mixed with a fourth of its bulk of sulphuric acid, and thrown upon a few drops of oil of turpentine, it occasions an explosive combustion of the oil. Sulphur digested in nitric acid at the boiling point is raised to its highest degree of oxidation and becomes sulphuric acid; iodine is also converted by it into iodic acid. Most vegetable and animal substances are converted by nitric acid into oxalic and carbonic acids. It stains the <sup>cuticle</sup> and nails of a yellow colour, and has the same effect upon wool; the orange

*Use the acid prepared.*  
 1. tin, acid,  
 water on igniting  
 2. charcoal  
 3. Oil of turp.  
 to alcohol

\* Annales de Chim. et de Phys. lxxiii. p. 418.

*Chc. ?*

patterns upon woollen table covers are produced by means of it. In the undiluted state it forms a powerful cautery.

In acting upon the less oxidable metals, such as copper and mercury, nitric acid is itself decomposed, and nitric oxide gas produced, which comes off with effervescence. Palladium and silver, when they are dissolved by the acid in the cold, produce nitrous acid in the liquor and evolve no gas, but this is very unusual in the solution of metals by nitric acid. Those metals, such as zinc, which are dissolved in diluted acids with the evolution of hydrogen, act in two ways upon nitric acid; sometimes they decompose it, so as to disengage a mixture of peroxide of nitrogen and nitric oxide, and at other times they decompose both water and nitric acid at once, in such proportions that the hydrogen of the water combines with the nitrogen of the acid to form ammonia, which last combines with another portion of acid, and is retained in the liquor as nitrate of ammonia. The protoxide of nitrogen is also evolved when zinc is dissolved in very feeble nitric acid, which may arise from the action of hydrogen upon nitric oxide. Nitric acid, in its highest state of

*Paper &  
gun cotton,  
candle -  
fire on  
sheet of letter  
paper.*

*Solution in  
acetic thus  
collodion.*

*Increasing  
about 70 per cent  
in weight.*

concentration, exerts no violent action upon certain organic substances, such as lignin or woody fibre and starch, for a short time, but unites with them and forms singular compounds. A proper acid for such experiments is procured with most certainty by distilling 100 parts of nitre, with no more than 60 parts of the strongest oil of vitriol. If paper is soaked for one minute in such an acid, and afterwards washed with water, it is found to shrivel up a little and become nearly as tough as parchment, and when dried to be remarkably inflammable, catching fire at so low a temperature as  $356^{\circ}$ , and burning without any nitrous odour (Pelouze.) Or if the strong undiluted nitric acid of commerce be mixed with an equal weight of oil of vitriol, and cotton wool be immersed in the mixture for a minute or two and afterwards washed with water, it is converted into gun-cotton, without injury to the cotton fibre (Schönbein).

Nitric acid forms an important class of salts, the nitrates, which occasion deflagration when fused with a combustible at a high temperature, from the oxygen in their acid, and are remarkable as a class for their general solubility, no <sup>neutral</sup> nitrate being insoluble in water. The nitrate of the black oxide of mercury is perhaps the least soluble of these salts. The nitrates of potash, soda, ammonia, baryta, and strontia, are anhydrous; but the nitrates of the extensive magnesian class of oxides all contain water in a state of intimate com-

bination, and have a formula analogous to that of hydrated nitric acid, or the nitrate of water itself. Of the four atoms of water contained in hydrated nitric acid of sp. gr. 1.42, one is combined with the acid as base, and may be named *basic* water, while the other three are in combination with the nitrate of water, and may be termed the *constitutional* water of that salt. The same three atoms of constitutional water are found in all the magnesian nitrates, with the addition often of another three atoms of water, as appears from the following formulæ:—

Nitric acid, 1.42.	. . .	. $\text{HO.NO}_5 + 3\text{HO}$
Prismatic nitrate of copper.	. . .	. $\text{CuO.NO}_5 + 3\text{HO}$
Rhomboidal nitrate of copper.	. . .	. $\text{CuO.NO}_5 + 3\text{HO} + 3\text{HO}$
Nitrate of magnesia.	. . .	. $\text{MgO.NO}_5 + 3\text{HO} + 3\text{HO}$

*A. N. Diction  
fluid acids  
water  
p. 76*

It is doubtful whether the proportion of constitutional water in any of these nitrates can be reduced below 3 atoms by heat without the loss of a portion of nitric acid at the same time, and the partial decomposition of the salt. The nitrates of the potash and magnesian classes do not combine together, and no double nitrates are known, nor nitrates with excess of acid. The nitrates with excess of metallic oxide, which are called *subnitrates*, appear to be formed on the type of the magnesian class: the subnitrate of copper, being  $\text{CuO.NO}_5 + 3\text{CuO.3HO}$  (Gerhardt), or nitrate of copper with 3 atoms hydrated oxide of copper. The water is strongly retained, and requires a temperature of  $300^\circ$  to expel it. The nitrate of red oxide of mercury is  $\text{HgO.NO}_5 + \text{HgO}$  (Kane).

Nitric acid in a solution cannot be detected by precipitating that acid in combination with any base, as the nitrates are all soluble, so that tests of another nature must be had recourse to, to ascertain its presence. A highly diluted solution of sulphate of indigo may be boiled without change, but on adding to it at the boiling temperature a liquid containing free nitric acid, the blue colour of the indigo is soon destroyed. If it is a neutral nitrate which is tested, a little sulphuric acid should be added to the solution, to liberate the nitric acid, before mixing it with the sulphate of indigo. It is also necessary to guard against the presence of a trace of nitric acid in the sulphuric acid. Another test of the presence of nitric acid has been proposed by De Richemont. The liquid containing the nitrate is mixed with rather more than an equal bulk of oil of

*Heat - first solution*

*Gold dissolves with HCl; not with HNO<sub>3</sub>*

*Dissolves a few grains.*

*Also Dr. Price's Let. Chem. Journal 1851. Lignite with alkali, so as to convert into a nitrite. Then distill the nitrous acid (SO<sub>2</sub> added) into solution iodide potassium containing a little starch. Iodine sulphurous acid comes over. Dehmann*



vitriol, and when the mixture has become cool, a few drops of a strong solution of protosulphate of iron are added to it. Nitric oxide is evolved, and combines with the protosulphate of iron, producing a rose or purple tint even when the quantity of nitric acid is very small. *One part of nitric acid in 24,000 of water has been detected in this manner.* Free nitric acid also is incapable of dissolving gold-leaf, although heated upon it, but acquires that property when a drop of hydrochloric acid is added to it. But in testing the presence of this acid, it is always advisable to neutralize a portion of the liquor with potash, and to evaporate so as to obtain the thin prismatic crystals of nitre, which may be recognised by their form, by their cooling nitrous taste, their power to deflagrate <sup>with</sup> combustibles at a red heat, and by the characteristic action of the acid they contain, when liberated by sulphuric acid, upon copper and other metals, in which ruddy nitrous fumes are produced.

*Becl.*  
*29 No. 5.*  
*Dec. 6, 1848*  
*p. 358*  
*Nov. 18*  
*1851*

If nitric acid be rigidly pure, it may be diluted with distilled water, and is not disturbed by nitrate of silver, nor by chloride of barium, the first of which discovers the presence of hydrochloric acid by producing a white precipitate of chloride of silver; the last discovers sulphuric acid by forming the white insoluble sulphate of baryta. The fuming nitric acid may be freed from hydrochloric acid, by retaining it warm on a sand-bath for a day or two, when the chlorine of the hydrochloric acid goes off as gas. To free it from sulphuric, it should be diluted with a little water, and distilled from nitrate of baryta; but the process for nitric acid which has been described gives it without a trace of sulphuric acid, when carefully conducted.

*Uses.*—Nitric acid is sometimes used in the fumigations required for contagious diseases, particularly in wards of hospitals from which the patients are not removed, the fumes of this acid being greatly less irritating than those of chlorine. For the purpose of fumigation, pounded nitre and concentrated sulphuric acid are used, being heated together in a cup. Nitric acid is par excellence the solvent of metals, and has other most numerous and varied applications not only in chemistry, but likewise in the arts and manufactures.



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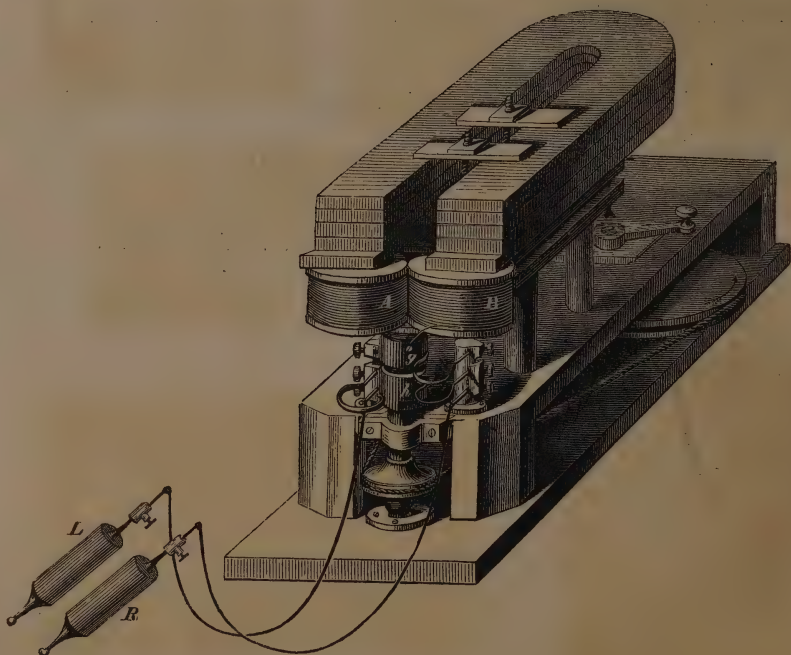
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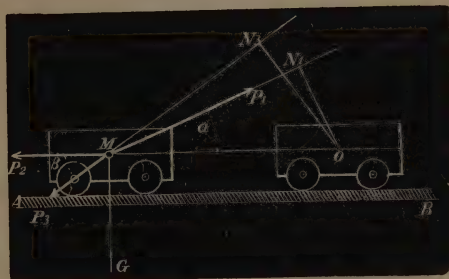
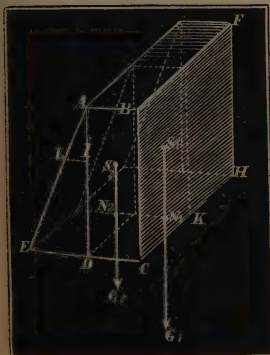
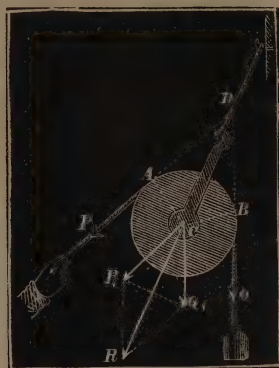
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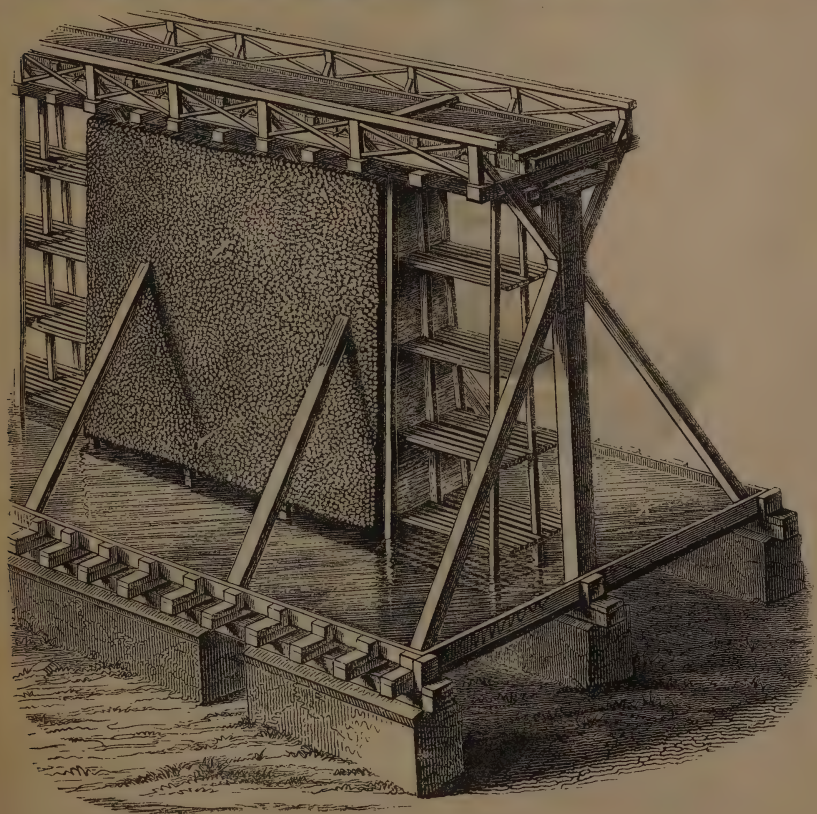
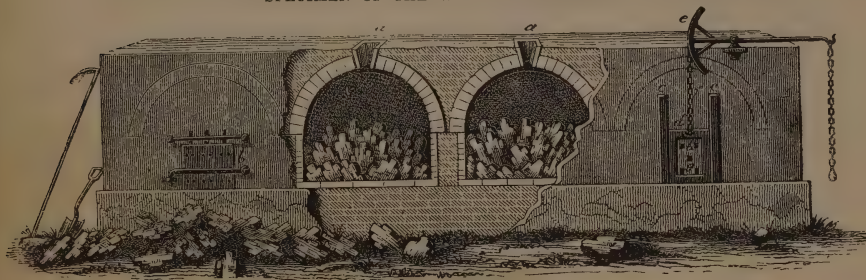
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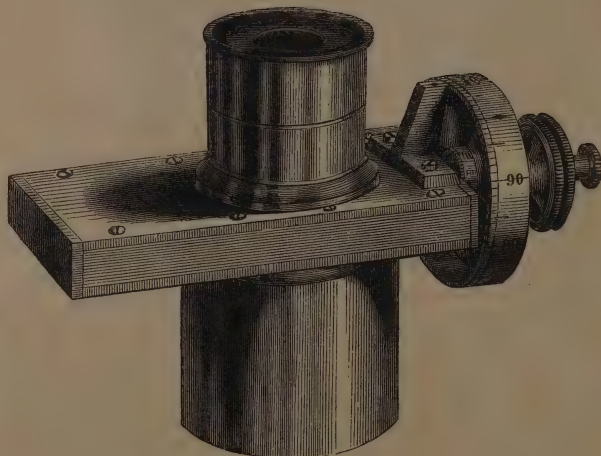
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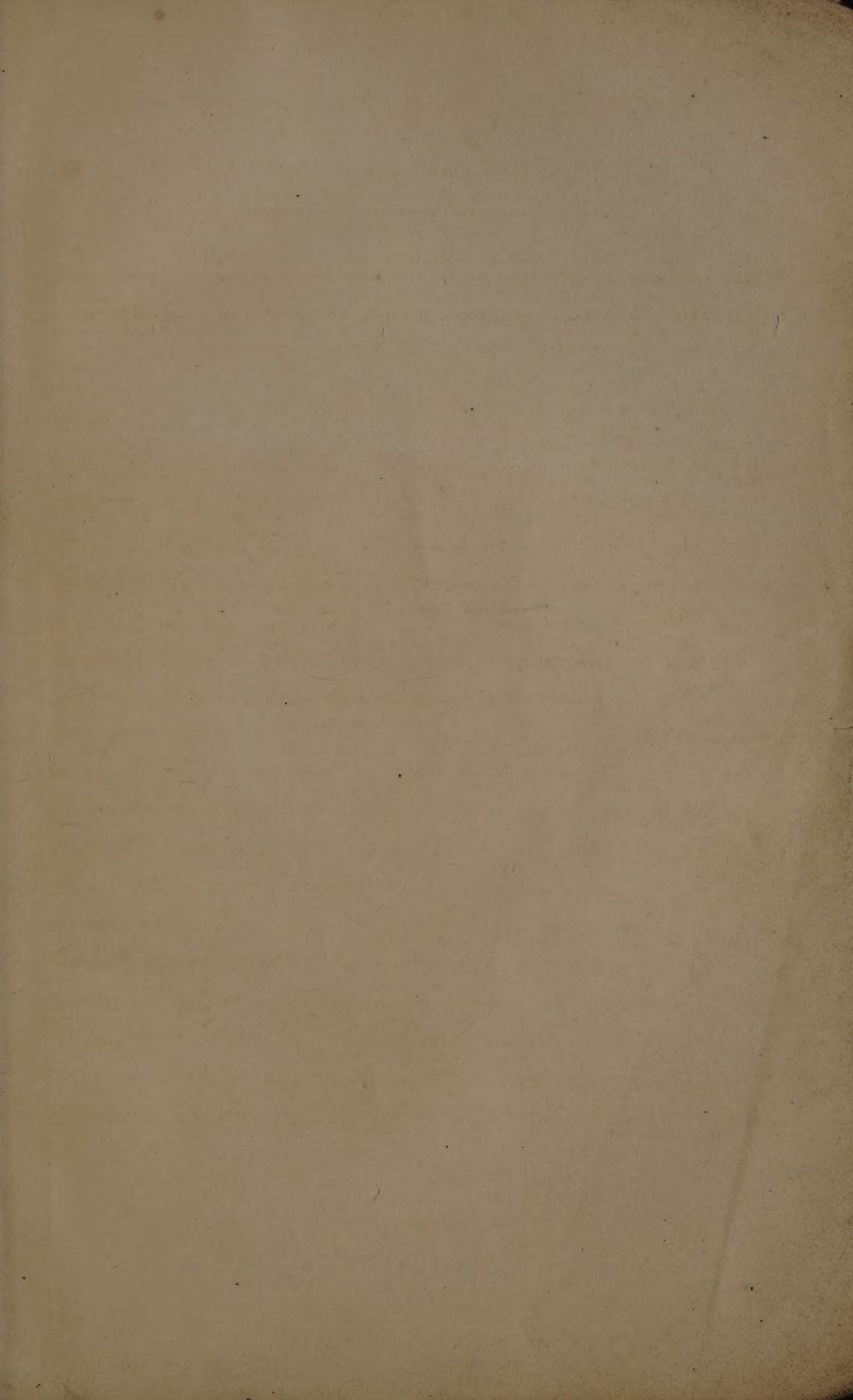
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